Synthesis, Molecular Structure and Reactivity of Di(1-cyclohepta-2,4,6-trienyl) thioether, $S(C_7H_7)_2$ and Tri(1-cyclohepta-2,4,6-trienyl) amine, $N(C_7H_7)_3$

Dissertation

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To

My Parents

To

Dr. Li Cui

Abbreviations

Å	Angström
ax	axial
^{t}Bu	*tert*-Butyl, $C(CH_3)_3$
°C	Degree Celsius
COSY	Correlated Spectroscopy
Cp	Cyclopentadienyl, η^5-C_5H_5
δ	chemical shift in ppm
Et	Ethyl
EI-MS	Electron Ionization-Mass Spectroscopy
Fig.	Figure
FD-MS	Field Desorption-Mass Spectroscopy
h	hour
Hz	Hertz
IR	Infrared Spectroscopy
λ	wave length
M	Metal
M^+	Metal ion
Me	Methyl, CH_3
mg	milligram
min	minute
ml	milliliter
mmol	millimole
m/e	mass/elemental electric charge
µl	microliter
NMR	Nuclear Magnetic Resonance
ν	frequency
Ph	Phenyl, C_6H_5
pm	picometer, 10^{-12} m
ppm	parts per million
r.t.	room temperature
THF	Tetrahydrofuran
thf	Tetrahydrofuran as a ligand
X	Halide

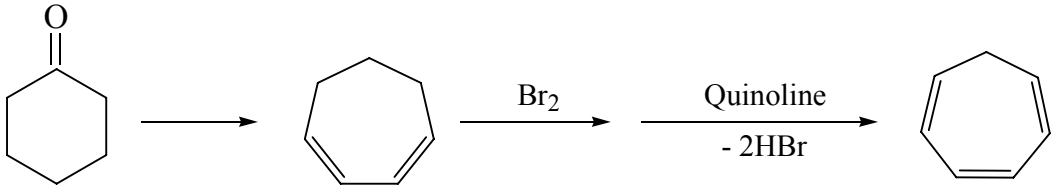
Contents

Chapter 1
Introduction

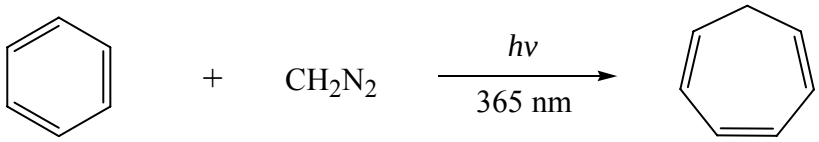
1.1 Cycloheptatriene (Tropilidene)

Synthesis of Cycloheptatriene, C_7H_8

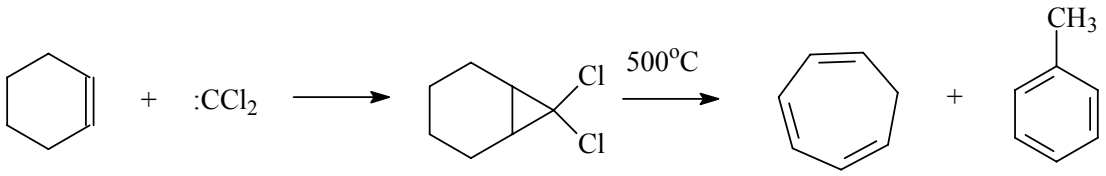
The preparation of cycloheptatriene was first achieved in 1939 by Kohler et al. using ring enlargement. According to their report, the seven-membered ring intermediate cycloheptanone was formed by ring expansion of cyclohexanone. Finally, cycloheptatriene was obtained from cyclohepta-1,3-diene by addition of bromine and subsequent dehydrobromination [1].



In 1950, Doering and Knox established the aromatic nature of tropones, tropolones and the tropylium ion. In their work on tropolone, they reported a more convenient method to prepare cycloheptatriene by photochemical reaction of diazomethane with benzene [2].



Later, another method for the preparation of cycloheptatriene was reported which involves heating 7,7-dichlorobicyclo[4,1,0]heptane, which had been prepared by addition of dichlorocarbene to cyclohexene [3].

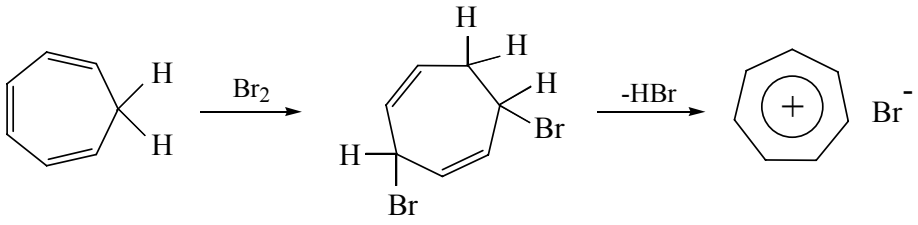


In the same year 1959, Nelson et al. found the synthesis of cycloheptatriene by solvolysis of the toluene-*p*-sulphonate of 1,4-dihydrobenzyl alcohol [4]. In addition, the reaction of acetylene with cyclopentadiene at 400 °C under pressure also gave cycloheptatriene [5]. Thermal treatment of bicyclo[2,2,1]hepta-2,5-diene made cycloheptatriene accessible on an industrial scale by the conversion of pure bicycloheptadiene to cycloheptatriene [6].

During the preparation of cycloheptatriene, toluene was often obtained as a by-product. It has been shown that toluene is formed by thermal rearrangement of cycloheptatriene [7].

Synthesis of the Tropylium Cation, $C_7H_7^+$

Among the many derivatives of cycloheptatriene, the tropylium ion attracted much attention because of its aromaticity and rich reactivity. Doering and Knox first reported the preparation of tropylium bromide by bromination and dehydrobromination of cycloheptatriene [8]. They treated tropilidene (C_7H_8) with one equivalent of bromine and, when they purified the liquid dibromide by distillation, a mass of crystals was obtained with a partial loss of hydrogen bromide. The material is strongly deliquescent, miscible with water and insoluble in non-polar organic solvents. It reacts immediately with aqueous silver nitrate producing an instantaneous precipitation of AgBr. This indicates the ionic character of this material.

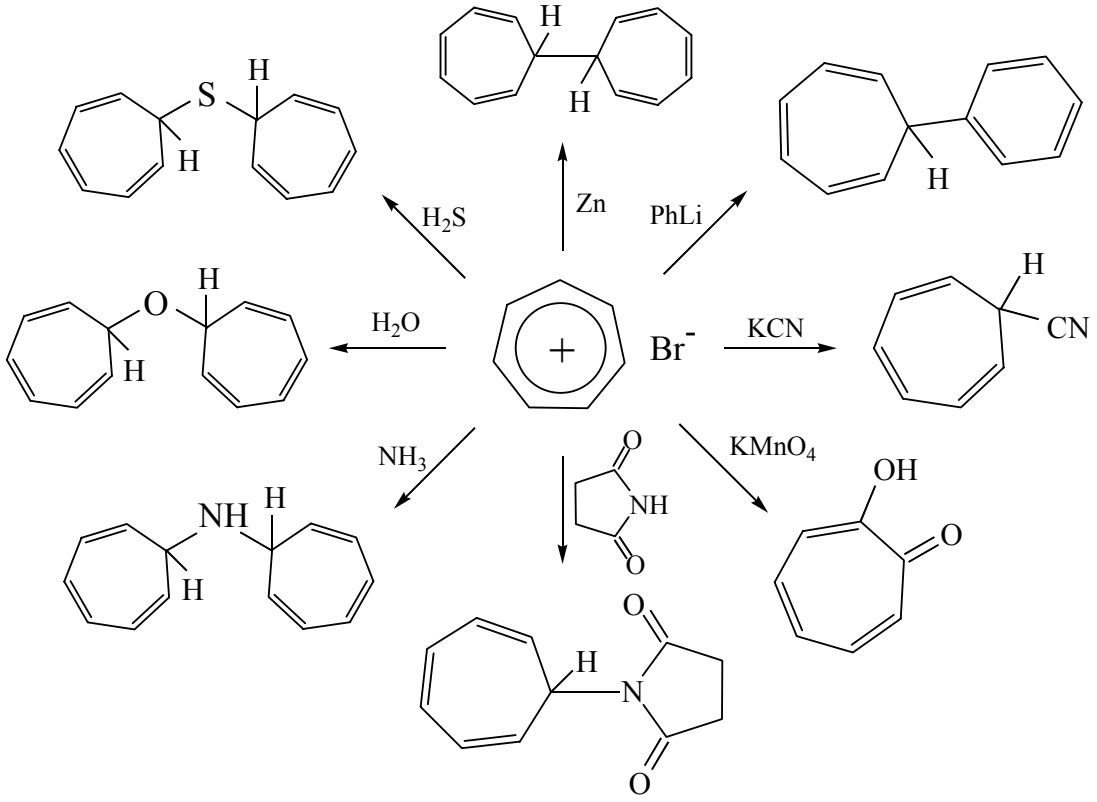


Later, a variety of other methods to prepare the tropylium ion from cycloheptatriene were reported, e.g. (1) abstraction of a hydride ion by carbenium ion sources such as triphenylmethyl salts [9]; (2) electrolytic oxidation [10]; (3) reaction

with boron tribromide [9b]; (4) γ-irradiation in the presence of *tert*-butyl bromide [11].

Starting from the tropylium cation, many compounds containing seven-membered rings could be prepared. The reduction of the tropylium ion with zinc dust affords ditropyl. Moreover, the tropylium ion reacts as an electrophilic reagent with the bases water, hydrogen sulfide and ammonia in aqueous solution to give di(1-cyclohepta-2,4,6-trienyl) ether, thioether and amine, respectively. The bases acetamide, benzamide and succinimide form N-tropyl derivatives, and the cyanide ion leads to tropyl cyanide [12].

The tropylium cation can be converted to tropolone, which is also aromatic, by treatment with alkaline permanganate solution [13].



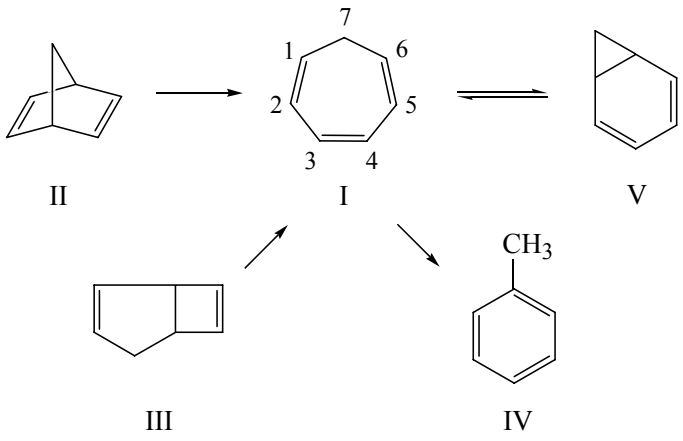
In earlier years, the cycloheptatriene molecule had been considered as aromatic because cycloheptatriene has six π electrons and seems to follow the 4n + 2 rule. But one of the seven carbon atoms is sp^3-hybridized, and the cycloheptatriene ring has a non-planar structure, as indicated by vibrational spectra [14], electron diffraction [15], microwave spectroscopy [16] and X-ray crystallographic analysis [17].

In contrast to cycloheptatriene, the cycloheptatrienylium (tropylium) cation is

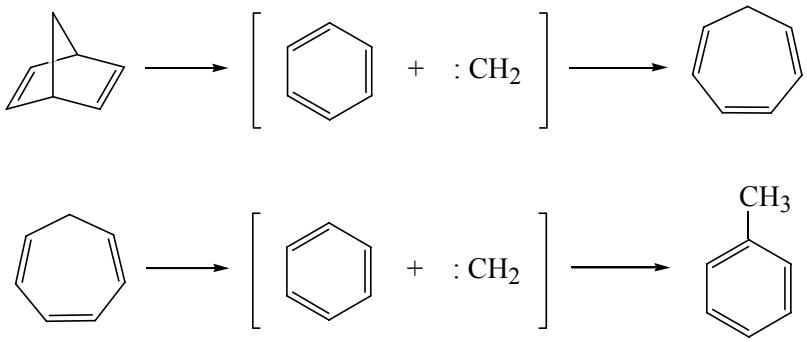
aromatic. The cycloheptatrienylium cation is obtained by removing a hydride ion from the sp^3 carbon atom, and the positively charged carbon becomes sp^2 which makes the ring planar. It still has six π electrons, and according to the Hückel Rule it is aromatic. This is why the carbon-bromine bond is not covalent. Because of the aromaticity, the degree of stabilization of the positive charge in the cation is large enough to overcome the normal tendency of the carbon-bromine bond to be covalent [8,18].

1.2 Cycloheptatriene Rearrangements

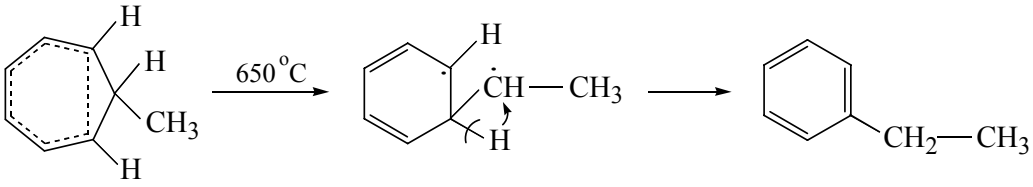
Tropilidene is connected to norbonadiene (II) [6,19], bicyclo[3.2.0]heptadiene (III) [20], toluene (IV) [6,19,21] and norcaradiene (V) [22] by thermal rearrangements. Intramolecular thermal transformations of the tropilidene skeleton to rearranged tropilidenes and 1,4-cyclohexadienes have also been reported [23].



As mentioned in the preparation of cycloheptatriene, toluene was often obtained as a by-product, which is formed under the influence of heat on cycloheptatriene [7]. The pyrolysis of tropilidene to give toluene was first observed by Woods [19a]. He found that when bicyclo[2,2,1]hepta-2,5-diene was heated to 450-475 °C under atmospheric pressure, cycloheptatriene was formed initially and subsequently rearranged to toluene. This was verified by pyrolysis of pure cycloheptatriene.



7-Methylcycloheptatriene was found to rearrange under pyrolysis at 650 °C to ethylbenzene, probably by the following reaction course [21].



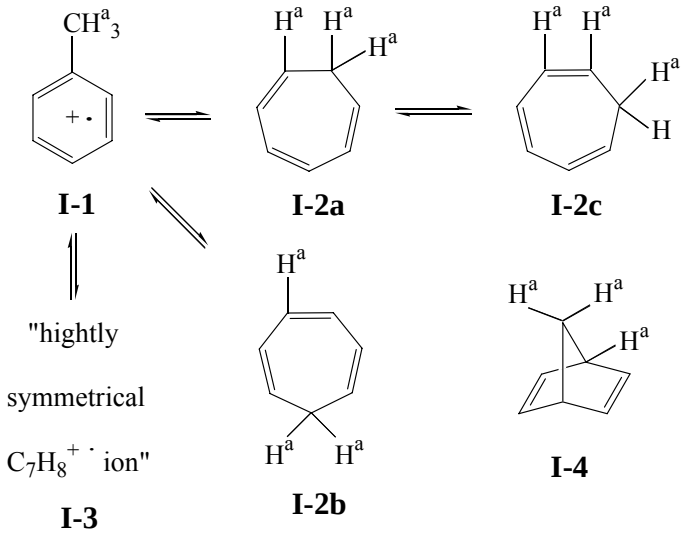
In 1963, Klump et al. carried out a kinetic study of the thermal isomerization of tropilidene to toluene in the gas phase and found a first-order rate constant [24]. They suggested that the bicyclic tautomer, norcaradiene, was the reactive intermediate. The kinetics of the bicyclo[2,2,1]heptadiene, toluene and cycloheptatriene isomerization were also studied by Herndon and co-workers, and a common intermediate was suggested for two of the three isomerizations [7a].

Theoretical calculations were also carried out for the rearrangement; in particular, the ab initio molecular orbital theory was applied to the cycloheptatriene-norcaradiene and related rearrangements [25]. Recently, multireference ab initio methods and density functional theory with a 6-31G* basis set have been applied by Jarzecki et al. to study the interconversions of norbornadiene, 1,3,5-cycloheptatriene, norcaradiene, and toluene [26]. Their calculations suggested that the route to the transition state for the formation of toluene from norcaradiene proceeds via a hydrogen transfer transition state that is formed directly from the Woodward-Hoffmann “allowed” transition state for the [1,5]carbon shift, but not from the “forbidden” transition state.

On the other hand, in mass spectrometry, the rearrangement of toluene and cycloheptatriene cations is one of the widely studied reactions. In 1957, Rylander et al. published [27] what has become a landmark in organic mass spectrometry: they suggested that the $C_7H_7^+$ ion formed from toluene by electron impact ionization had

the seven-membered ring tropylium ion structure.

A number of detailed studies, some using multiple isotopic labeling, have shown that the decomposition of toluene [28-30] and cycloheptatriene [29,31] molecular ions can involve the loss of all positional identity of the carbon as well as the hydrogen atoms, *i.e.* atom scrambling took place in these reactions. A common suggestion for the behavior of the toluene and the isomeric cycloheptatrienylium cation is that their molecular rearrangements involve isomerization to a common structure such as cycloheptatriene (**I-2a** or **I-2b**) [32] or a more symmetrical ion (**I-3**) [33] with hydrogen scrambling in **I-2a** involving H migration through **I-2c** [32,34,35]. The observation [31] that norbornadiene (**I-4**) undergoes loss of C_2H_2 with only minor carbon scrambling makes this a less probable intermediate for the isomerization of either **I-1** or **I-2**.

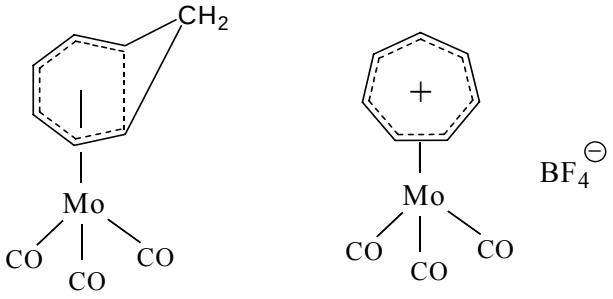


Lifshitz reviewed the historical background for the understanding of the unimolecular dissociation of the gas-phase toluene radical cation [36]. And in a recent study [37], a theoretical calculation using the minimum energy reaction pathway (MERP) method and experimental studies were used to investigate the ring walk of methylene groups in toluene radical cations.

1.3 Transition Metal Complexes of Cycloheptatriene

Two decades after the first preparation of cycloheptatriene, Wilkinson et al. prepared the first η^6-cycloheptatriene complex, $Mo(\eta^6\text{-}C_7H_8)(CO)_3$, in 1958 [38], and its crystal structure was determined by X-ray diffraction by Dunitz and Pauling two

years later [39]. In the same year 1958, shortly after the preparation of $Mo(\eta^6\text{-}C_7H_8)(CO)_3$, the first η^7-cycloheptatrienyl complex, $[Mo(\eta^7\text{-}C_7H_7)(CO)_3][BF_4]$ was synthesized by Dauben and co-workers [40].

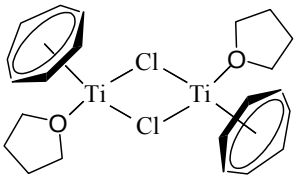


In 1959, the development of the synthesis, the structure and the reactivity of the cycloheptatriene complexes was incorporated in a review by Green and Ng [41]. Various complexes containing a transition metal bonded to a seven-membered ring system have been synthesized. Many of the early cycloheptatriene compounds are cycloheptatriene-carbonyl complexes, such as $M(\eta^6\text{-}C_7H_8)(CO)_3$ (M = Cr [38], Mo [42], W [43,44]) and $Fe(\eta^4\text{-}C_7H_8)(CO)_3$ [45]. A large number of $\eta^7\text{-}C_7H_7$ tropylium halfsandwich (e.g. $V(\eta^7\text{-}C_7H_7)(CO)_3$ [46]) and sandwich complexes have been described, such as $M(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)$ (M = Ti [47,48], Zr [49], Hf [49], V [47], Cr [50], Mo [51], W [51]) and $M(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5R_5)$ (M = Ti, Zr, Hf, R = H or Me) [52,53]. Related sandwich compounds of η^6-cycloheptatriene are also known, such as $M(\eta^6\text{-}C_7H_8)(C_5H_5)$ (M = V [54], Fe [55], Mn [56], Cr [57]).

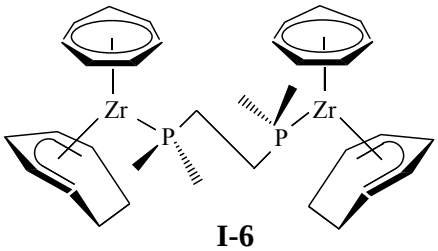
Many different methods are available to prepare cycloheptatriene complexes. The displacement of carbonyl groups from hexacarbonyl complexes by cycloheptatriene is the traditional method. Most of the earlier tricarbonyl cycloheptatriene [38,42-45] or cycloheptatrienyl [46] complexes were obtained in this way. Condensation of metal atoms in the presence of an excess of cycloheptatriene is a versatile method to prepare low-valent metal complexes. For example, condensation of Mn atoms with cycloheptatriene in the presence of CO gives $Mn(\eta^4\text{-}C_7H_8)_2(CO)$ [58], and sandwich compounds of the type $M(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)$ (M = Ti [47,48], Zr [49], Hf [49], V [47], Cr [50], Mo [51], W [51]) have also been prepared by this method. Reduction of metal halides in the presence of cycloheptatriene is another commonly used method to synthesize low-valent metal complexes. Fischer et al. first reported the reduction of $CrCl_2$, $MoCl_2$ and WCl_6 in the presence of cycloheptatriene and cyclopentadiene, producing mixed sandwich compounds $M(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)$ (M = Cr, Mo, W)

[57,59]. The mixed sandwich compounds $M(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5R_5)$ (M = Ti, Zr, Hf, R = H or Me) [52,53] could also be obtained by treatment of cyclopentadienyl metal chlorides with appropriate reducing agents in the presence of cycloheptatriene.

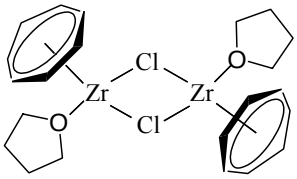
With the development of the cycloheptatriene complex chemistry, some more complicated structures were identified. Some complexes have a bridged structure such as **I-5** [60], **I-6** and **I-7** [61], and **I-8** [62,67].



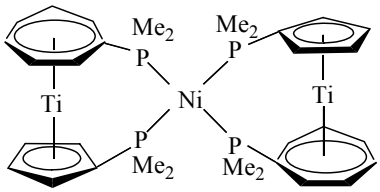
I-5



I-6

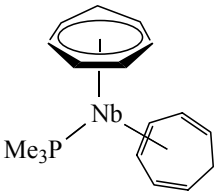


I-7

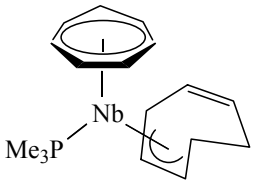


I-8

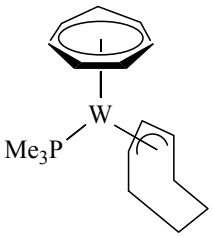
Several complexes were prepared with an open sandwich structure such as **I-9** [63], **I-10** [64], **I-11** and **I-12** [65], and **I-13** [66].



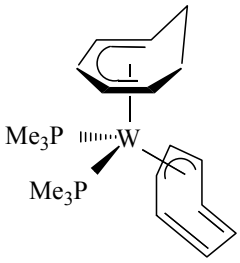
I-9



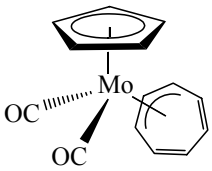
I-10



I-11

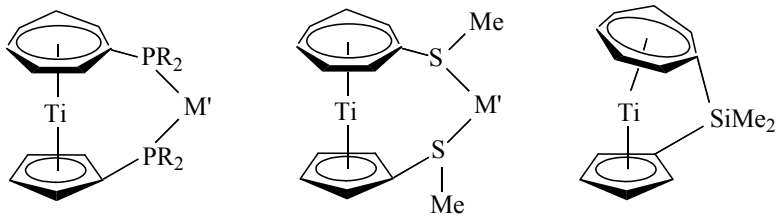


I-12



I-13

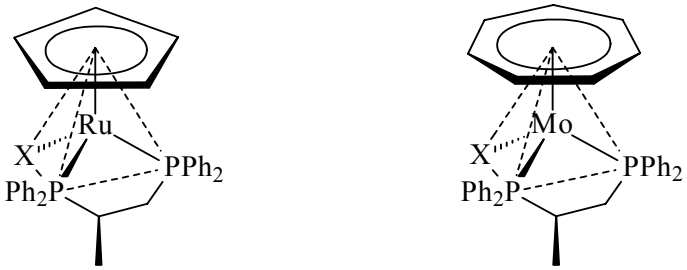
In addition, a few examples with a closed sandwich structure were reported, such as **I-14** [67], **I-15** and **I-16** [68].



M' = $Cr(CO)_4$, $Mo(CO)_4$, $PtCl_2$

I-14 **I-15** **I-16**

More recently, chiral-at-metal compounds containing the versatile 18-electron cycloheptatriene molybdenum unit were prepared [69]. In these complexes the metal atom is the only center of chirality. The stereochemistry of the ruthenium complexes (η^5-C_5H_5)Ru(prophos)X [70] was compared with the corresponding molybdenum compounds (η^7-C_7H_7)Mo(prophos)X (X = $NCMeBF_4$, Cl, I, CN, H, Me) [71].



1.4 Transition Metal Complexes with Thioether Ligands

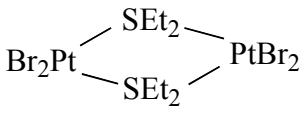
Platinum complexes with simple dialkyl sulfides or with more than one thioether ligand were studied in the early years of 20th century by the Russian school around Tschugajeff [72]. The isomers **I-17** and **I-18** were among the first compounds reported (R = alkyl, aryl).

I-17 **I-18**

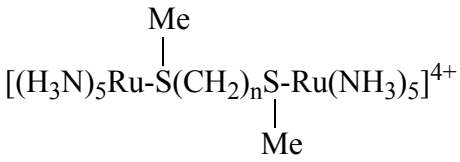
Another example of dialkylsulfide complexes is the series of compounds $Cl_3M(SEt_2)_3$ with M = Rh, Ir, Ru [73,74]. The diethyl thioether ligands can be easily replaced by either pyridine or aniline.

Typical examples of dinuclear complexes are compounds containing bidentate $RS(CH_2)_nSR$ and tridentate $[RS(CH_2)_n]_2S$ ligands. A series of mononuclear Ru compounds had been prepared and characterized by Chatt et al. [73].

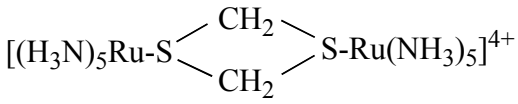
Because there are two nonbonding electron pairs available at the sulfur atom, thioethers may also act as bridging ligands. The following examples (**I-19** [75], **I-20** [76], **I-21** [76] and **I-22** [77]) have been reported.



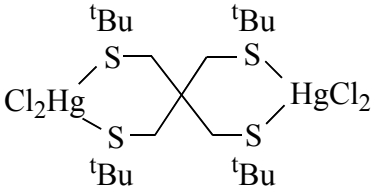
I-19



I-20

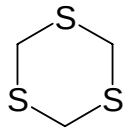


I-21

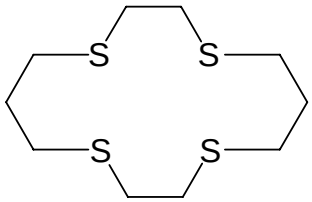


I-22

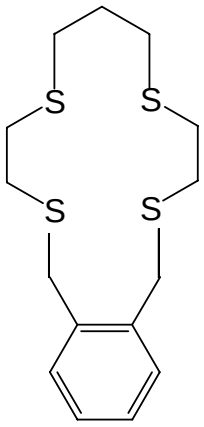
A large group of thioether ligands are the macrocyclic thioethers. Typical examples of cyclicpoly-thioether ligands are shown below (A-E). These macrocyclic poly-thioethers possess very flexible coordination behavior.



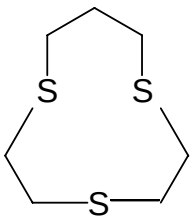
A



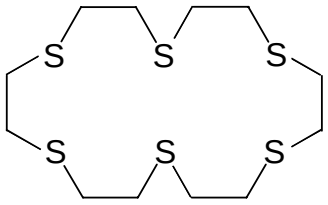
C



E

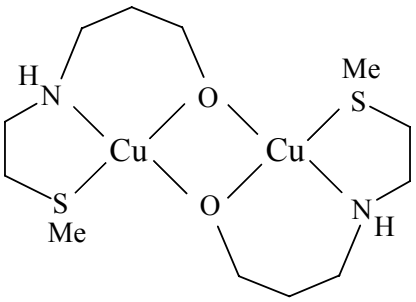


B



D

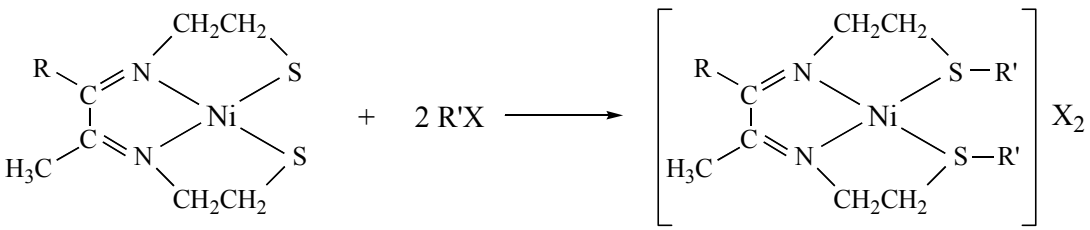
Thioether ligands which contain, in addition to the sulfur, one or more other donor atoms, e.g. nitrogen or oxygen, are also known. Representative examples of this kind of ligand have been reported by Schugar et al. [78]. The copper complex given below is an example of a dinuclear system employing three different donor atoms in the complex formation [79].



Thioether complexes are, in general, obtained in a direct reaction from aqua or halogeno complexes with the thioether in aqueous or alcoholic solutions, by simple addition or substitution. A series of Nb^{IV} compounds, NbX_4L and NbX_4L_2, have been reported [80], where for L = Me_2S in benzene solution an equilibrium between the five- and the six-coordinate species was detected. The stability of the bis-adduct with respect to the mono-adduct decreases in the order X = I > Br > Cl.

Another related system has been investigated by Flint et al. [81], who reacted finely ground $Ni(ClO_4)_2$·aq directly with 2,5-dithiahexane for several weeks and then treated further with the ligand until the ν(OH) absorption of water could no longer be detected in the IR spectrum.

A different route is the S-alkylation of thiolato ligands, as for example in the reaction of (diethyl-2-mercaptoethylamine) gold(III) with bromoethane to give the corresponding thioether complex [82]. S-Alkylation of a mercaptoamine complex of Ni^{II} (**I-23**) with alkyl halides in DMF solution gave the thioether complex (**I-24**) [83].



I-23 **I-24**

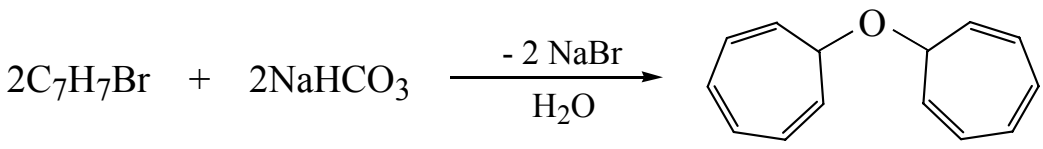
Chapter 2
Investigations with
Di(1-cyclohepta-2,4,6-trienyl) thioether, $S(C_7H_7)_2$

The η-cyclopentadienyl (η^5-C_5R_5) and η-arene (η^6-C_6R_6) ring systems belong to the most common class of ligands encountered in organotransition metal chemistry. Transition metal complexes with these ligands have been studied extensively, and many have contributed to the development of areas such as homogeneous catalysis, organic synthesis, new materials and biological or medical science. Although cycloheptatriene (η^6-C_7H_8) and cycloheptatrienyl (η^7-C_7H_7) transition metal complexes have been known for over three decades, surprisingly, the chemistry of these ligands has been little studied in comparison with that of cyclopentadienyl and arene ligands [41].

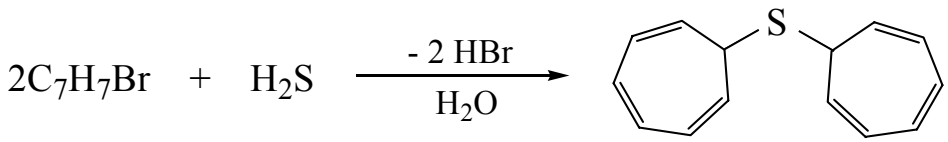
In addition, due to the lone pairs of the heteroatoms, organic derivatives of group-16 elements have attracted much attention. Quite a lot of work has been done on diphenyl ethers, in which the group-16 heteroatoms (O, S, Se) act as bridge between two phenyl groups. Although dicycloheptatrienyl ether and dicycloheptatrienyl thioether, which contain two seven-membered rings, were known for over four decades, only very little chemistry has been reported.

2.1 Synthesis

Di(1-cyclohepta-2,4,6-trienyl) ether, $(C_7H_7)_2O$, was first obtained by Doering and Knox in 1954 [8]. Thermal elimination of hydrogen bromide from dibromotropilidene produces cycloheptatrienylium bromide (tropylium bromide), C_7H_7Br. In agreement with its salt-like properties the compound is soluble in water. The treatment of its aqueous solution with sodium bicarbonate produces di(1-cyclohepta-2,4,6-trienyl) ether.

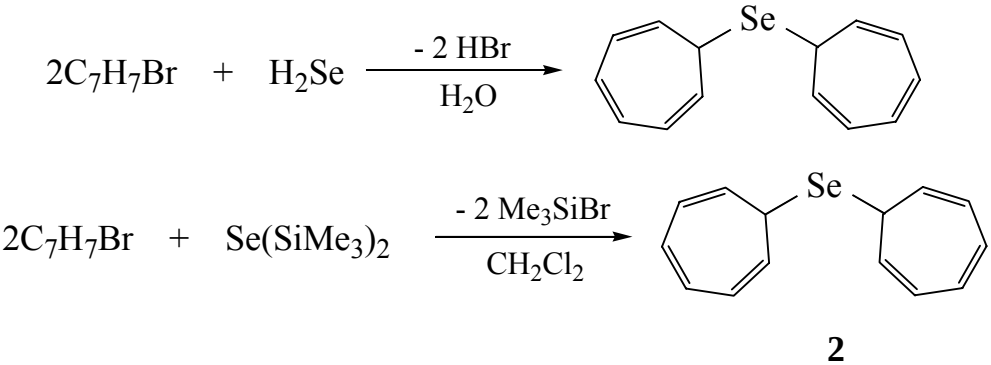


In a later investigation [12], Doering and Knox studied the reactions of the cycloheptatrienylium (tropylium) ion and prepared the di(1-cyclohepta-2,4,6-trienyl) thioether, $(C_7H_7)_2S$ (**1**), from tropylium bromide and the gas hydrogen sulfide.



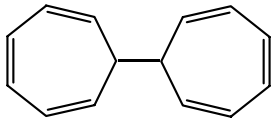
1

The synthesis of di(1-cyclohepta-2,4,6-trienyl) selenoether, $(C_7H_7)_2Se$ (**2**), reported in the literature [84], was similar to the preparation of $(C_7H_7)_2O$ and $(C_7H_7)_2S$ (**1**), involving the reaction of tropylium bromide with hydrogen selenide (H_2Se) gas. The gas H_2Se was obtained by hydrolysis of aluminum selenide [85], but some modifications had to be made due to the instability and toxicity of H_2Se. In order to avoid the problems arising from the unstable and toxic gas H_2Se, in our work, we used an in-situ source of H_2Se, *i.e.* bis(trimethylsilyl)selenide, $Se(SiMe_3)_2$, in analogy to the preparation of tri(1-cyclohepta-2,4,6-trienyl) phosphane [86] from $P(SiMe_3)_3$. By this method hydrogen selenide gas itself was not involved in the reaction and the selenium compound **2** was kept dissolved in the solution. Thus, the problems involved in the old preparation were avoided successfully. The new method is easy to operate and gives satisfactory yields (~90 %).



2

1,1'-Di(1-cyclohepta-2,4,6-trienyl) ("ditropyl"), $(C_7H_7)_2$ (**3**), was also prepared according to Doering and Knox's work [12]. Tropylium bromide was reduced using zinc dust in water, and after work-up a colorless crystalline product was isolated.

$$2C_7H_7Br + Zn \xrightarrow[H_2O]{-\ 2\ ZnBr}$$ 

3

The above cycloheptatrienyl derivatives of group-16 elements and also ditropyl were all prepared from the starting compound tropylium bromide, C_7H_7Br. The tropylium compounds are interesting because the theory of aromaticity has ascribed relative stability to conjugated unsaturated cycles having six π-electrons in a ring. The best known example is benzene, which contains a six-membered ring. For the eight-membered ring, cyclooctatetraene, although it has been synthesized, a non-planar structure has been found, and it is not aromatic [87].

Between the six-membered ring and the eight-membered ring is the seven-membered ring. In earlier studies the cycloheptatriene molecule (C_7H_8) had been considered to be aromatic, as having the proper number of 6 π-electrons, but it is not aromatic because the hybridization of one of the carbon atoms in the ring is sp^3 and not sp^2. In the presence of mild reducing agents such as lithium, a hydride ion can easily be removed from the sp^3 carbon of cycloheptatriene to create a tropylium carbocation which is planar. This cycloheptatrienylium (tropylium) cation is aromatic and stable [88]. Therefore, tropylium bromide behaves like a salt rather than a covalent compound. It is soluble in water and ethanol, but insoluble in non-polar organic solvents.

Childs et al. [89] have reported the structure of the salt ditropylium ether bis(trifluoromethanesulfonate). The cation contains two equivalent seven-membered (C_7H_6) rings, each of which bears a positive charge (Fig. 1). The seven-membered rings in the cation are not completely planar but are present in a very shallow boat conformation. The conformation can be defined in terms of three planes, *i.e.* C(2)C(1)C(7) (**A**)**,** C(2)C(3)C(6)C(7) (**B**)**,** and C(3)C(4)C(5)C(6) (**C**), with the angles between these planes being **A-B** (α) 2.7(5)° and **B-C** (β) 3.9(5)°. In addition to the bending of the ring, the oxygen atom is significantly protruding out of the C(2)C(1)C(7) plane. The oxygen can be regarded as being in a pseudo-equatorial position of the very shallow boat conformation of the seven-membered rings. The rings may still remain their aromatic character in the ditropylium ether salts.

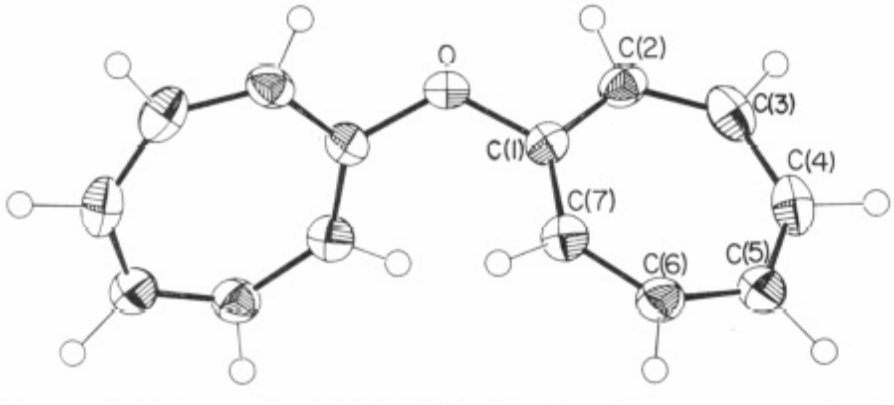


Fig.1. The structure of the cation in the
ditropylium ether bis(trifluoromethanesulfonate) salt [89]

But the neutral molecules di(1-cyclohepta-2,4,6-trienyl) ether, thioether and selenoether have no longer aromatic rings. The X-ray structure analysis of the di(1-cyclohepta-2,4,6-trienyl) thioether, $S(C_7H_7)_2$ (**1**), and the Diels-Alder adduct of **1** with maleic anhydride (see below) reveal that the seven-membered ring is not planar.

NMR-Spectroscopic Characterization

The ^1H and ^{13}C NMR data of the cycloheptatrienyl derivatives of the group 16 elements are summarized in Table 1, which also includes cycloheptatriene and ditropyl (**3**) for comparison. As may be seen from the proton NMR data of the different compounds, a small chemical shift variation is observed for proton H^1 which is close to the bridge atoms. Thus, $\delta(H^1)$ is 3.76 in di(1-cyclohepta-2,4,6-trienyl) ether, 3.45 in the sulfane (**1**) and 4.10 in the selane (**2**). The olefinic part (H^2-H^7) of the cyclohepta-2,4,6-trienyl (C_7H_7) system shows little change. The spectrum consists of four different signals with an integral ratio 1:2:2:2. The chemical shift of the protons at the 1-position of C_7H_8 and $(C_7H_7)_2$ were observed at higher magnetic field by more than 1 ppm compared with those at the corresponding position of the group 16 derivatives, $E(C_7H_7)_2$ (E = O, S (**1**) and Se (**2**)). In the ^{13}C NMR spectra, four different carbons are observed for the cycloheptatrienyl substituent. The C^1 atoms which connect directly to the bridge heteroatoms are dramatically shifted upfield. In agreement with the "heavy atom effect", the chemical shift of C^1 in the

di(1-cyclohepta-2,4,6-trienyl) group 16 compounds, $E(C_7H_7)_2$, changes from 75.1 ppm (E = O) to 42.3 ppm (E = S) and 37.3 ppm (E = Se).

Table 1. NMR spectroscopic data of the cyclohepta-2,4,6-trienyl compounds [a), b)]

	C_7H_8	$O(C_7H_7)_2$	$S(C_7H_7)_2$ **1**	$Se(C_7H_7)_2$ **2**	$(C_7H_7)_2$ **3**
^{1}H-NMR					
$\delta(H^1)$	2.11t (2H)	3.76t (2H)	3.45t (2H)	4.10t (2H)	2.02s (2H)
$\delta(H^2, H^7)$	5.16m (2H)	5.53m (4H)	5.35m (4H)	5.46m (4H)	5.20m (4H)
$\delta(H^3, H^6)$	6.08m (2H)	5.89dt (4H)	5.96dt (4H)	5.86m (4H)	6.13dt (4H)
$\delta(H^4, H^5)$	6.46m (2H)	6.40t (4H)	6.35t (4H)	6.17m (4H)	6.54t (4H)
^{13}C-NMR					
$\delta(C^1)$	28.2	75.1	42.3	37.3 [60] [c)]	42.5
$\delta(C^2, C^7)$	120.7	122.4	125.3	127.0	125.1
$\delta(C^3, C^6)$	126.9	125.6	126.4	127.7	126.1
$\delta(C^4, C^5)$	131.2	130.8	131.5	132.2	131.2
^{77}Se-NMR				535.3	

a) Measured in C_6D_6 at 25 ºC.

b) NMR Multiplicities: s singlet, d doublet, dt doublet of triplets, t triplet, m multiplet.

c) Coupling constant, [^1J(Se,C)][Hz].

All the data in Table 1 were measured in C_6D_6 at 25 °C. Later we generally used $CDCl_3$ as the NMR solvent in order to compare the NMR data in the same solvent. But, unfortunately, the NMR data of $Se(C_7H_7)_2$ in $CDCl_3$ were not available because of its decomposition. Naturally occurring selenium contains the isotope ^{77}Se, which possesses a nuclear magnetic moment (I = 1/2) that makes it suitable for NMR measurements. But low natural abundance (7.5 %) and low sensitivity (6.97×10^{-3} relative to that of protons at constant field) made it difficult to obtain ^{77}Se NMR spectra. Several ways to improve the sensitivity can be considered. An increase of the sample volume can increase the number of nuclei suitable for the experiment, and extension of the scanning time can improve the signal to noise ratio. For di(1-cyclohepta-2,4,6-trienyl) selenoether (**2**), ^{77}Se NMR measurements gave a shift of 535.3 ppm (Table 1).

In order to compare the NMR data of di(1-cyclohepta-2,4,6-trienyl) thioether, $S(C_7H_7)_2$ (**1**), with those of its complexes (see below), we also measured the NMR spectra of $S(C_7H_7)_2$ in $CDCl_3$. The data are listed in Table 2.

Table 2. NMR spectroscopic data of $S(C_7H_7)_2$ (1) [a), b)]

^{1}H-NMR		^{13}C-NMR	
$\delta(H^1)$	3.61t (2H)	$\delta(C^1)$	41.6
$\delta(H^2, H^7)$	5.48m (4H)	$\delta(C^2, C^7)$	124.7
$\delta(H^3, H^6)$	6.22dt (4H)	$\delta(C^3, C^6)$	126.4
$\delta(H^4, H^5)$	6.58t (4H)	$\delta(C^4, C^5)$	131.2

a) Measured in $CDCl_3$ at 25 ºC.

b) NMR Multiplicities: t triplet, dt doublet of triplets, m multiplet.

Molecular Structure of Di(1-cyclohepta-2,4,6-trienyl) thioether, $S(C_7H_7)_2$ (1)

A single crystal of di(1-cyclohepta-2,4,6-trienyl) thioether, $S(C_7H_7)_2$ (**1**), was obtained by slow solvent evaporation from a concentrated diethyl ether solution in the refrigerator (-28 °C). The molecular structure of **1** is shown in Fig. 3. The relevant distances and angles of the inner sphere are compiled in Table 4; the numbering system is also given in Fig. 3.

The (chiral) molecules $S(C_7H_7)_2$ (**1**) possess a two-fold axis (C_2) through the sulfur atom; both ring substituents assume the boat conformation with the sulfur attached to an axial position. The axial connection differs from that observed in the lattice of $N(C_7H_7)_3$ (where all 3 C_7H_7 substituents are attached to N in equatorial position) and of $P(C_7H_7)_3$ (where the ratio equatorial : axial is 2:1 [86]). Compared with the tri(1-cyclohepta-2,4,6-trienyl) compounds of N and P, the angles α and β in **1** (cf. Fig. 2) (α = 41.9° and β = 21.8°) which characterize the bending of the 1-cyclohepta-2,4,6-trienyl substituents are considerably reduced in the lattice of $S(C_7H_7)_2$ (**1**) (cf. α = 54.2° (av.) and β = 26.5° (av.) in $N(C_7H_7)_3$ (**24**); α = 55.7° (av.), β = 27.0° (av.) for equatorial C_7H_7 substituents and α = 46.2° (av.), β = 23.6° (av.) for axial C_7H_7 substituents in $P(C_7H_7)_3$) (Table 3).

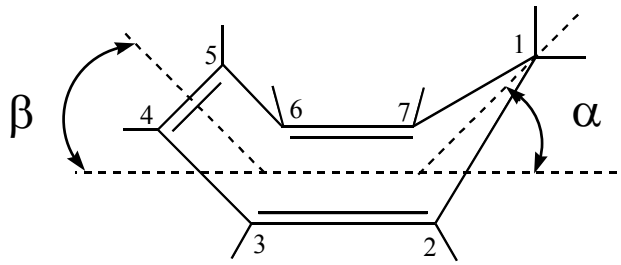


Fig.2. Conformation of the 1-cyclohepta-2,4,6-trienyl substituent [86]

Table 3. Comparison of the angles α and β in 1-cyclohepta-2,4,6-trienyl compounds

	$N(C_7H_7)_3$ **24**	$P(C_7H_7)_3$	$[P(C_7H_7)_4]^+BF_4^-$	$S(C_7H_7)_2$ **1**	$S(C_7H_7)(C_7H_7{\cdot}C_4H_2O_3)$ **4a**	**4a'**
α (°)	54.2 (av.) (equatorial)	55.7 (av.) (2 equatorial)	58.3 (av.) (2 equatorial)			
		46.2 (av.) (1 axial)	39.4 (av.) (2 axial)	41.9 (axial)	29.4 (axial)	28.6 (axial)
β (°)	26.5 (av.) (equatorial)	27.0 (av.) (2 equatorial)	28.7 (av.) (2 equatorial)			
		23.6 (av.) (1 axial)	21.4 (av.) (2 axial)	21.8 (axial)	14.3 (axial)	13.7 (axial)

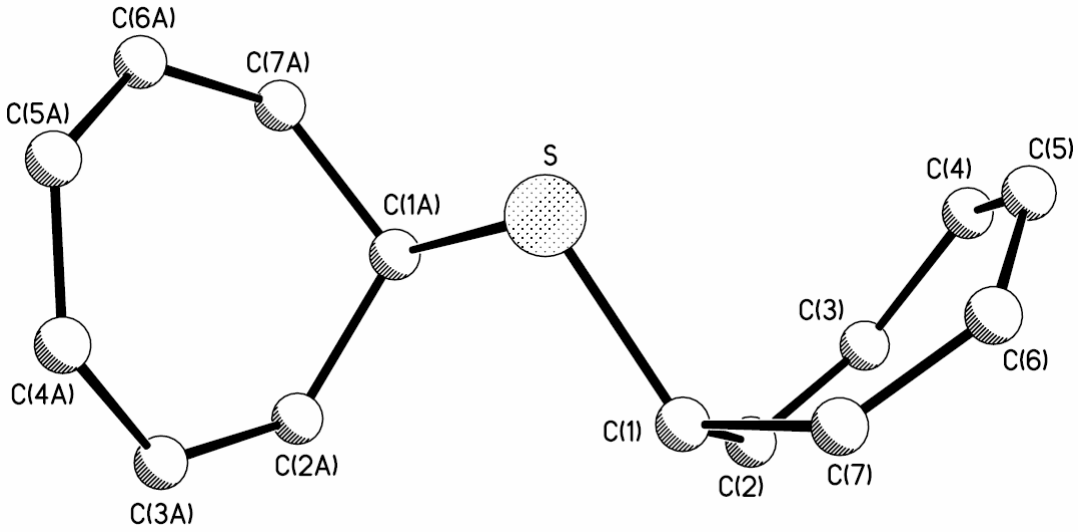


Fig.3. Molecular structure of di(1-cyclohepta-2,4,6-trienyl) thioether, $S(C_7H_7)_2$ (**1**)

Table 4. Relevant distances and angles of $S(C_7H_7)_2$ (1) [a)]

Distances (pm)		Angles (°)	
S-C(1A)	184.43(18)	C(1A)-S-C(1)	100.71(12)
S-C(1)	184.43(18)	C(7)-C(1)-C(2)	111.80(16)
C(1)-C(7)	149.3(3)	C(7)-C(1)-S	107.98(13)
C(1)-C(2)	149.9(3)	C(2)-C(1)-S	113.84(13)
C(2)-C(3)	133.7(3)	C(3)-C(2)-C(1)	125.03(18)
C(3)-C(4)	144.1(3)	C(2)-C(3)-C(4)	127.09(19)
C(4)-C(5)	133.0(3)	C(5)-C(4)-C(3)	126.1(2)
C(5)-C(6)	142.0(3)	C(4)-C(5)-C(6)	126.7(2)
C(6)-C(7)	131.7(3)	C(7)-C(6)-C(5)	127.78(19)
		C(6)-C(7)-C(1)	125.85(18)
Dihedral angles (°)			
α [b)]	41.9		
β [b)]	21.8		

a) Symmetry transformation used to generate equivalent atoms (A): -x, y, -z + 1/2.

b) The dihedral angles α = C(1,2,7)/C(2,3,6,7) and β = C(2,3,6,7)/C(3,4,5,6) define the bending of the cyclohepta-2,4,6-trienyl ring (cf. Fig. 2).

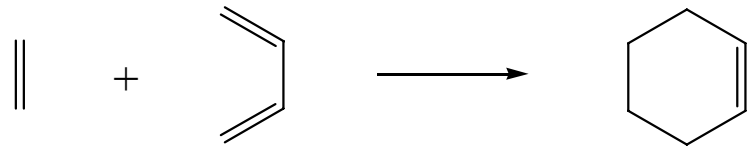
The diffraction data and the refinement parameters for **1**, which were calculated from the X-ray structure analysis, are shown in Table 5.

Table 5. Crystal data and structure refinement for $S(C_7H_7)_2$ (1)

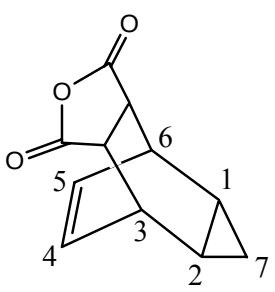
Empirical formula	$C_{14}H_{14}S$	
Formula weight	214.31	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*C*2/c	
Unit cell dimensions	a = 19.110(4) Å	α = 90°
	b = 5.9283(12) Å	β = 129.20(3)°
	c = 13.542(3) Å	γ = 90°
Volume	1189.0(4) $Å^3$	
Z	4	
Density (calculated)	1.197 Mg/m^3	
Absorption coefficient	0.236 mm^{-1}	
F(000)	456	
Crystal size	0.28 x 0.18 x 0.13 mm^3	
θ range for data collection	2.75 to 25.99°	
Index ranges	-23<h<22, -7<k<6, -16<l<16	
Reflections collected	3968	
Independent reflections	1149 [R(int) = 0.0304]	
Completeness to θ = 24.99°	98.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1149 / 0 / 69	
Goodness-of-fit on F^2	1.022	
Final R indices [I > 2σ (I)]	R1 = 0.0368, wR2 = 0.1054	
R indices (all data)	R1 = 0.0428, wR2 = 0.1097	
Largest diff. peak and hole	0.145 and -0.187 e.$Å^{-3}$	

2.2 Diels-Alder Reactions of $S(C_7H_7)_2$

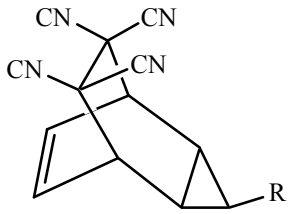
The Diels-Alder reaction is considered to be one of the most useful reactions in organic chemistry. It is essentially a cycloaddition reaction in which an alkene adds to a 1,3-diene to form a six-membered ring.



Cyclic conjugated trienes and their derivatives, when reacted with dieneophiles, generally produce Diels-Alder adducts. In 1939, Kohler et al. [1] prepared an adduct of cycloheptatriene (C_7H_8) with maleic anhydride in refluxing xylene. The structure of this compound was assigned in 1953 by Alder and Jacobs as *endo*-*cis*-3,6-*endo*-cyclopropyl-1,2,3,6-tetrahydrophthalic anhydride (Fig. 4a) [90]. Jordan and Elliott extended the Diels-Alder reactions of cycloheptatriene, and new adducts were synthesized from the dienophile tetracyanoethylene with tropilidene and tropylacetylacetone (Fig. 4b) [91]. In addition, Wahl and Weiss reported the Diels-Alder adduct of ditropyl and dimethyl acetylenedicarboxylate (Fig. 4c) [92].

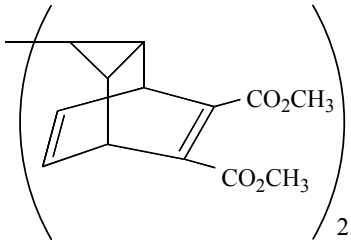


a



R = H, -CH(COCH$_3$)$_2$

b



c

Fig.4. Diels-Alder products reported in earlier work [90-92]

Since the first preparation [12] of di(1-cyclohepta-2,4,6-trienyl) thioether, $S(C_7H_7)_2$ (**1**), in 1957, only very few literature concerning this compound has appeared. In 1992, Kuhrau and Stadler reported Diels-Alder reactions [93] in which a mixture of ditropyl (**3**) and di(1-cyclohepta-2,4,6-trienyl) thioether (**1**) reacted with bis(4-(1,2,4-triazoline-3,5-dione-4-yl)phenyl)methane (BPMTD) to produce soluble copolymers via repetitive Diels-Alder polyaddition (Fig. 5).

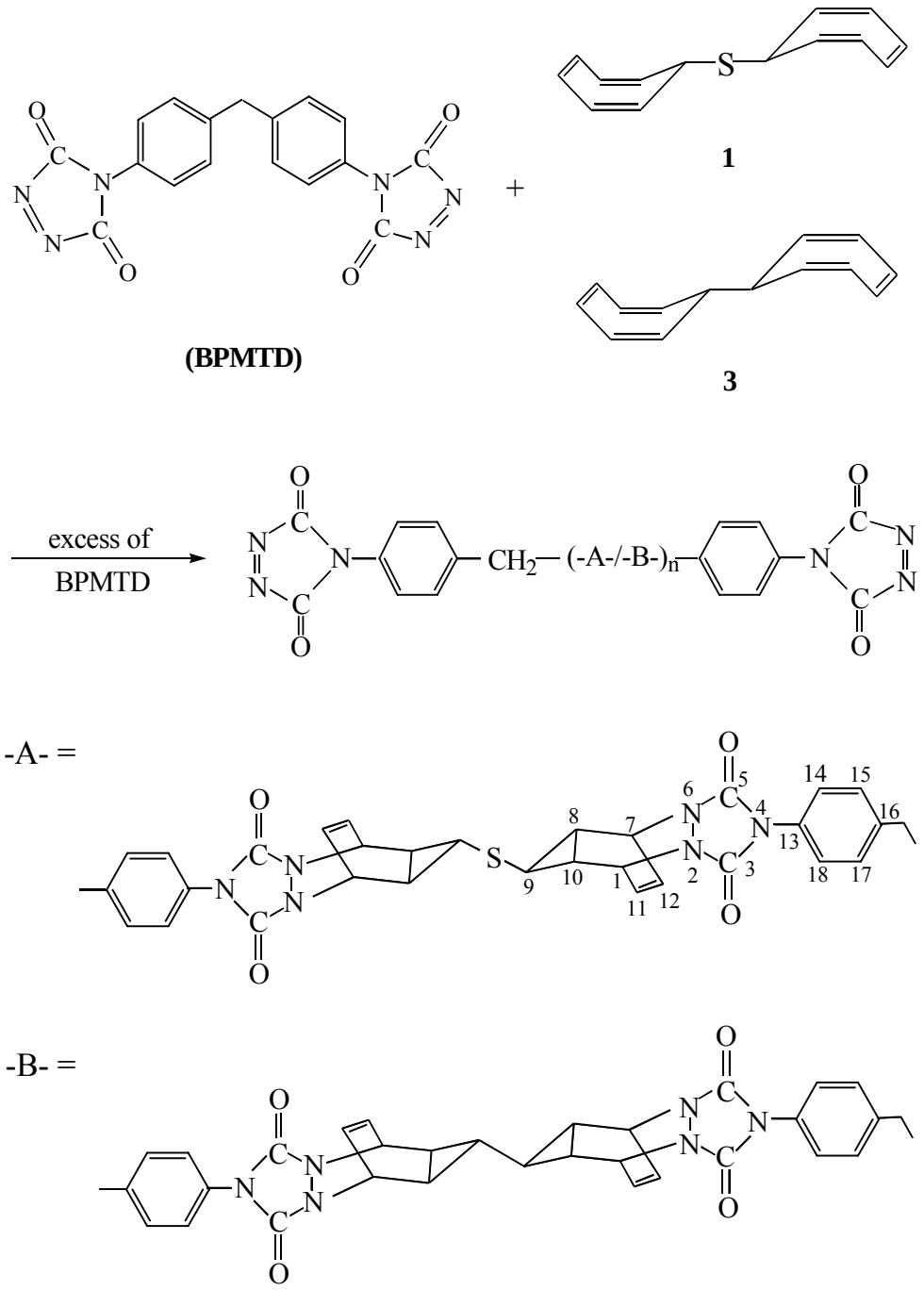


Fig.5. Reaction scheme for copolymerization reactions of ditropyl and di(1-cyclohepta-2,4,6-trienyl) thioether with BPMTD [93]

Refluxing di(1-cyclohepta-2,4,6-trienyl) thioether, $S(C_7H_7)_2$ (**1**), in THF solution in the presence of maleic anhydride led to the expected Diels-Alder reaction (Fig. 6). We changed the ratio of maleic anhydride to $S(C_7H_7)_2$ (**1**) from 1 over 2 to 4 and expected to obtain different adducts, but only the 1:1 adduct **4a** was obtained which was isolated as light yellow crystals. The structure of **4a** has been confirmed by X-ray structure analysis (see below). Under the same reaction conditions, di(1-cyclohepta-2,4,6-trienyl) thioether, $S(C_7H_7)_2$ (**1**), reacted with maleimide or N-phenyl maleimide to give the corresponding 1:1 Diels-Alder adducts **4b** and **4c**, respectively, which were isolated as white powders.

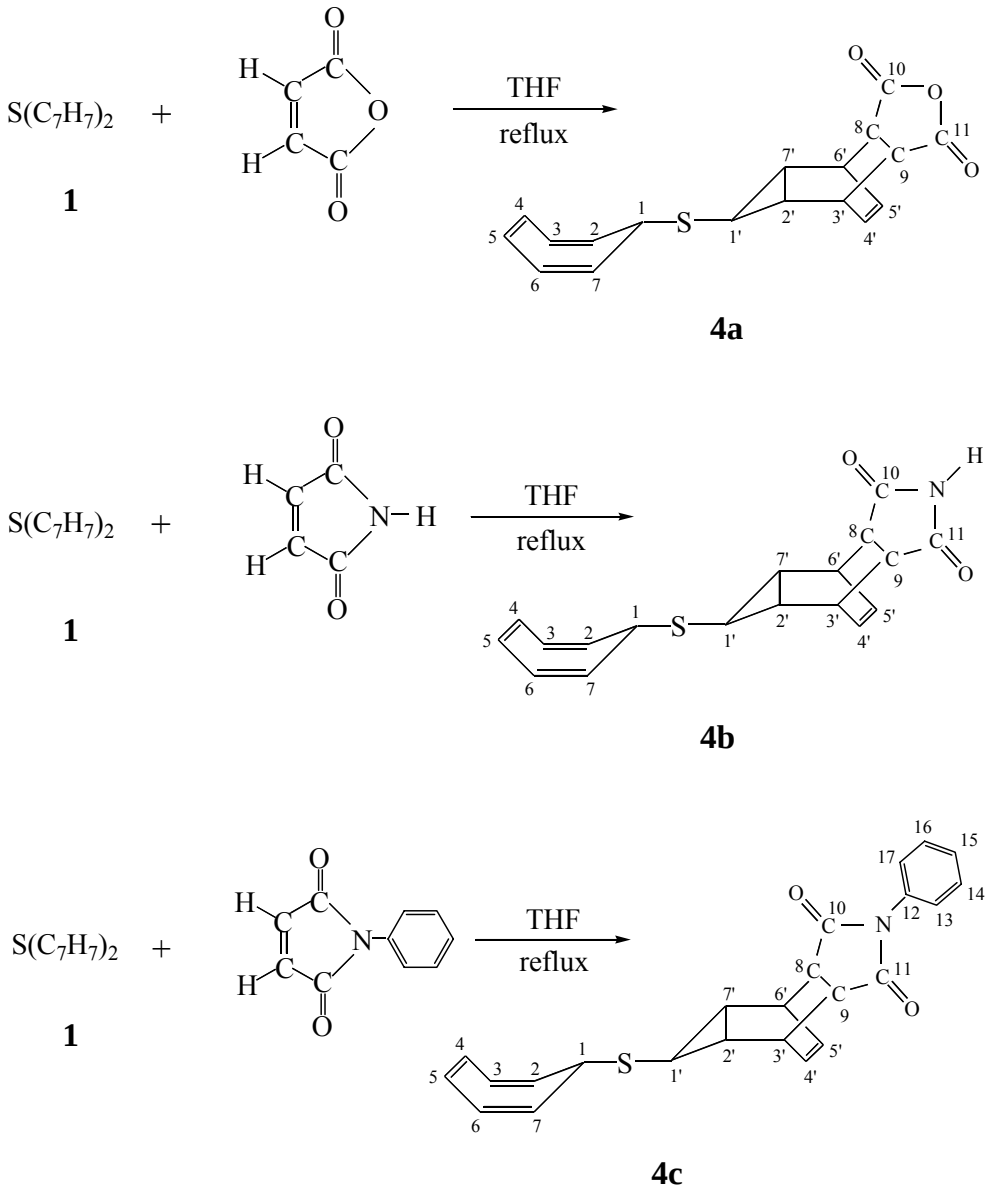


Fig.6. Synthesis of the Diels-Alder adducts **4a**, **4b** and **4c**

NMR-Spectroscopic Characterization

For the compound **4a**, a total of nine ^{1}H NMR signals (*i.e.* 4 originating from the unchanged ring, 4 from the modified ring and 1 from the maleic anhydride unit) and ten ^{13}C NMR signals are observed (Table 6).

The close analogy of the ^{1}H NMR and ^{13}C NMR spectra of the products **4a**, **4b** and **4c** provides strong evidence that the Diels-Alder 1:1 additions proceed in the same way when di(1-cyclohepta-2,4,6-trienyl) thioether (**1**) reacts with maleic anhydride, maleimide and N-phenyl maleimide. The spectra of the products are very similar except that of the product **4c** which contains the extra signals of the phenyl. The products contain only one cycloheptatrienyl ring which has reacted, whereas the other ring is unchanged. For the unreacted cycloheptatrienyl ring, chemical shifts of the protons show a slight variation by less than 0.15 ppm compared with those at the corresponding positions of di(1-cyclohepta-2,4,6-trienyl) thioether (**1**). The substituted ring has changed to the norcaradienyl isomer with a triangle attached to the sulfur atom. This is evident in particular from the high-field shift of the signals assigned to the "aliphatic" positions $H^{1'}$, $H^{2'}$ and $H^{7'}$. The protons of $H^{3'}$, $H^{6'}$ and H^8, H^9 also shift to higher magnetic field because new bonds were formed between the carbons of $C^{3'}$, $C^{6'}$ and C^8, C^9. In addition, the chemical shifts of $H^{4'}$ and $H^{5'}$ also changed to higher magnetic field due to the disappearance of the double bonds between $C^{2'}$, $C^{3'}$ and $C^{6'}$, $C^{7'}$. In the carbon NMR spectra the same effects were observed. This provides strong evidence that the Diels-Alder reactions took place as expected.

Table 6. NMR data of the Diels-Alder adducts 4a, 4b and 4c (cf. Fig. 6) [a), b)]

	4a	**4b**	**4c**
^{1}H-NMR			
$\delta(H^1)$	3.69t (1H)	3.67t (1H)	3.70t (1H)
$\delta(H^2, H^7)$	5.47m (2H)	5.48t (2H)	5.50t (2H)
$\delta(H^3, H^6)$	6.17m (2H)	6.17m (2H)	6.17m (2H)
$\delta(H^4, H^5)$	6.45t (2H)	6.45s (2H)	6.46s (2H)
$\delta(H^{1'})$	1.64t (1H)	1.64t (1H)	1.69t (1H)
$\delta(H^{2'}, H^{7'})$	1.32t (2H)	1.30m (2H)	1.37t (2H)
$\delta(H^{3'}, H^{6'})$	3.20m (2H)	3.42s (2H)	3.55m (2H)
$\delta(H^{4'}, H^{5'})$	5.92m (2H)	5.83m (2H)	5.89m (2H)

$\delta(H^8, H^9)$	3.50t (2H)	2.95s (2H)	3.09t (2H)
δ(NH)		8.14s (1H)	
δ(NPh)			7.37m (3H), 7.12m (2H)
^{13}C-NMR			
$\delta(C^1)$	44.1	44.0	44.1
$\delta(C^2, C^7)$	124.3	124.5	124.5
$\delta(C^3, C^6)$	127.2	127.1	127.1
$\delta(C^4, C^5)$	131.2	131.1	131.2
$\delta(C^{1'})$	17.8	17.5	17.4
$\delta(C^{2'}, C^{7'})$	19.9	20.3	20.5
$\delta(C^{3'}, C^{6'})$	33.4	33.2	33.7
$\delta(C^{4'}, C^{5'})$	129.2	128.4	128.65
$\delta(C^8, C^9)$	45.2	45.9	44.6
$\delta(C^{10}, C^{11})$	171.7	178.1	177.1
$\delta(C^{12})$			131.7
$\delta(C^{13}, C^{17})$			126.4
$\delta(C^{14}, C^{16})$			129.1
$\delta(C^{15})$			128.55

a) NMR data in $CDCl_3$ at 25 °C.

b) NMR Multiplicities: s singlet, d doublet, dt doublet of triplets, t triplet, m multiplet.

Molecular Structure of the Diels-Alder Adduct 4a

A single crystal of **4a** was obtained by slow solvent evaporation from a concentrated diethyl ether solution. The structure of the Diels-Alder adduct **4a** was unambiguously established by X-ray analysis. The molecular structure of **4a** is shown in Fig. 7. It contains an unchanged cyclohepta-2,4,6-trienyl ring and a ring involved in the Diels-Alder reaction. The relevant distances and angles of the inner sphere are compiled in Table 7; the numbering system is given in Fig. 7. All bond distances and angles are normal and correspond to the established structure.

The unit cell of the adduct contains two types of independent molecules (**4a** and **4a'**, ratio 1:1) which have only slightly different bond distances and angles. As shown in **4a** and **4a'** for the unchanged ring, the average bond distance of S-C(1) (185.1(4) pm) is nearly the same as the corresponding bond length in di(1-cyclohepta-2,4,6-trienyl) thioether (184.43(18) pm). The angle at the sulfur atom

is close to the value expected for sulfanes, *i.e.* 100.71(12)° in **1** and slightly larger in the Diels-Alder adduct (103.20(19)° in **4a** and 102.72(18)° in **4a'**). Comparable angles have been determined by various methods for simple sulfanes such as $S(CH_3)_2$ (98.52(10)° by microwave spectroscopy [94]), $S(CD_3)_2$ (98.0(3)° by neutron powder diffraction [95]), $S(CF_3)_2$ (105.6 ± 3° by electron diffraction [96]) and $S(CN)_2$ (96° by X-ray structure analysis [97]); cf. SH_2 92.3° [98].

The substituted ring involving C(8) is present in the norcaradienyl form with a nearly equilateral triangle attached to the sulfur atom; the transannular distance C(9)-C(16) (151.2(5) pm) corresponds to a single bond. New bonds were formed between the carbons of the original maleic anhydride moiety and the carbons of the original cycloheptatrienyl ring involved in the reaction, C(10)-C(11) as well as C(14)-C(15). Correspondingly, the bond lengths of C(9)-C(10) (151.7(6) pm) and of C(15)-C(16) (153.1(6) pm) correspond to a single bond. The bond length of C(17)-C(18) (131.6(5) pm) remains characteristic of a double bond. In addition, the distance of S-C(8) (177.1(4) pm) is shorter than that of S-C(1) (185.0(4) pm), probably because the cycloheptatrienyl ring changed to the norcaradienyl isomer. The shape of the reacted ring has changed due to the substitution. The bond angles C(8)-C(16)-C(15) (121.9(3)°) and C(8)-C(9)-C(10) (122.6(3)°) are slightly smaller than the corresponding bond angles C(1)-C(2)-C(3) (128.6(5)°) and C(1)-C(7)-C(6) (128.5(5)°) in the unchanged cyclohepta-2,4,6-trienyl ring. The bond angles C(16)-C(15)-C(17) (110.4(3)°) and C(9)-C(10)-C(18) (110.9(3)°) are considerably smaller than the corresponding bond angles C(2)-C(3)-C(4) (128.5(5)°) and C(7)-C(6)-C(5) (128.9(6)°). Therefore, the substituted ring is more bent than the unchanged cyclohepta-2,4,6-trienyl ring. Compared with di(1-cyclohepta-2,4,6-trienyl) thioether, $S(C_7H_7)_2$ (**1**), the remaining C_7H_7 ring is even further flattened if maleic anhydride is added to **1** (Table 3).

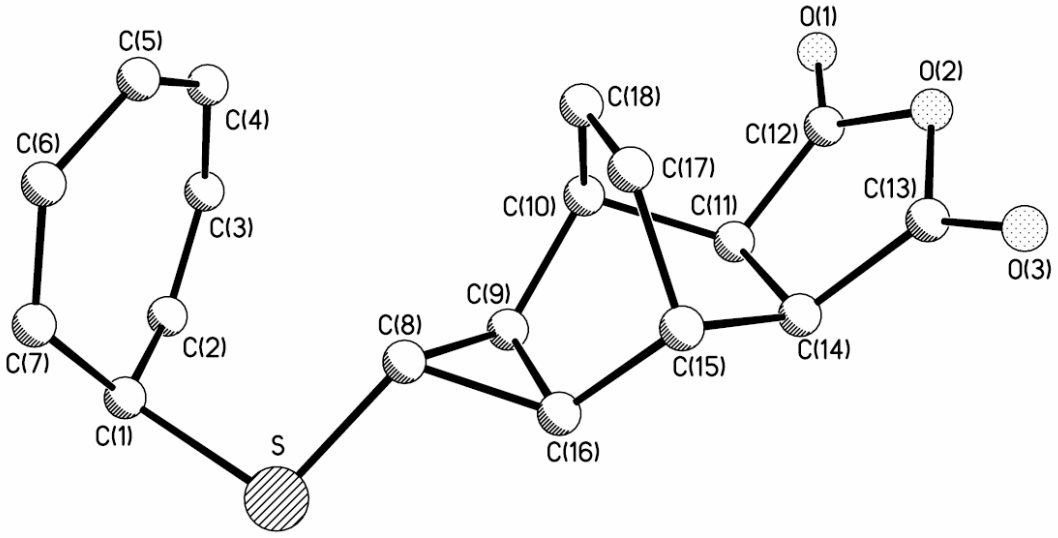


Fig.7. Molecular structure of the compound **4a**

Table 7. Relevant distances and angles of 4a and 4a' [a)]

Distances (pm)		Distances (pm)	
S-C(8)	177.1(4)	S'-C(8')	177.1(4)
S-C(1)	185.0(4)	S'-C(1')	185.2(4)
O(1)-C(12)	120.2(5)	O(1')-C(12')	119.2(5)
O(2)-C(12)	137.8(5)	O(2')-C(13')	138.0(5)
O(2)-C(13)	139.0(5)	O(2')-C(12')	139.6(5)
O(3)-C(13)	119.3(5)	O(3')-C(13')	118.9(5)
C(1)-C(7)	146.2(7)	C(1')-C(7')	147.9(6)
C(1)-C(2)	147.3(7)	C(1')-C(2')	149.2(6)
C(2)-C(3)	132.5(8)	C(2')-C(3')	132.9(6)
C(3)-C(4)	143.1(9)	C(3')-C(4')	143.2(8)
C(4)-C(5)	131.8(10)	C(4')-C(5')	133.3(8)
C(5)-C(6)	138.3(11)	C(5')-C(6')	141.7(8)
C(6)-C(7)	133.1(9)	C(6')-C(7')	131.9(7)
C(8)-C(16)	151.0(5)	C(8')-C(9')	149.9(6)
C(8)-C(9)	151.4(5)	C(8')-C(16')	150.1(6)
C(9)-C(16)	151.2(5)	C(9')-C(16')	149.1(5)
C(9)-C(10)	151.7(6)	C(9')-C(10')	152.3(5)
C(10)-C(18)	149.5(6)	C(10')-C(17')	150.0(6)
C(10)-C(11)	157.0(5)	C(10')-C(11')	156.2(6)

C(11)-C(12)	147.7(6)	C(11')-C(12')	149.6(6)
C(11)-C(14)	154.4(5)	C(11')-C(14')	152.5(6)
C(13)-C(14)	149.8(6)	C(13')-C(14')	150.8(5)
C(14)-C(15)	156.0(5)	C(14')-C(15')	155.0(6)
C(15)-C(17)	150.2(6)	C(15')-C(18')	149.1(6)
C(15)-C(16)	153.1(6)	C(15')-C(16')	153.4(5)
C(17)-C(18)	131.6(5)	C(17')-C(18')	132.2(6)
Angles (°)		Angles (°)	
C(8)-S-C(1)	103.20(19)	C(8')-S'-C(1')	102.72(18)
C(12)-O(2)-C(13)	110.0(3)	C(12')-O(2')-C(13')	110.5(3)
C(7)-C(1)-C(2)	116.5(4)	C(7')-C(1')-C(2')	116.7(4)
C(7)-C(1)-S	112.0(3)	C(7')-C(1')-S'	113.0(3)
C(2)-C(1)-S	112.9(3)	C(2')-C(1')-S'	110.5(3)
C(3)-C(2)-C(1)	128.6(5)	C(3')-C(2')-C(1')	127.6(4)
C(2)-C(3)-C(4)	128.5(5)	C(2')-C(3')-C(4')	129.6(5)
C(5)-C(4)-C(3)	126.5(6)	C(5')-C(4')-C(3')	127.1(5)
C(4)-C(5)-C(6)	129.0(7)	C(4')-C(5')-C(6')	127.7(5)
C(7)-C(6)-C(5)	128.9(6)	C(7')-C(6')-C(5')	128.8(5)
C(6)-C(7)-C(1)	128.5(5)	C(6')-C(7')-C(1')	129.5(4)
C(16)-C(8)-C(9)	60.0(2)	C(16')-C(8')-C(9')	59.6(3)
C(16)-C(8)-S	114.9(3)	C(16')-C(8')-S'	117.2(3)
C(9)-C(8)-S	118.3(3)	C(9')-C(8')-S'	121.1(3)
C(16)-C(9)-C(8)	59.9(2)	C(16')-C(9')-C(8')	60.3(3)
C(16)-C(9)-C(10)	110.4(3)	C(16')-C(9')-C(10')	110.6(3)
C(8)-C(9)-C(10)	122.6(3)	C(8')-C(9')-C(10')	122.1(3)
C(18)-C(10)-C(9)	110.9(3)	C(18')-C(10')-C(9')	110.6(3)
C(18)-C(10)-C(11)	107.6(3)	C(18')-C(10')-C(11')	106.0(3)
C(9)-C(10)-C(11)	103.5(3)	C(9')-C(10')-C(11')	104.6(3)
C(12)-C(11)-C(14)	104.0(3)	C(12')-C(11')-C(14')	104.7(3)
C(12)-C(11)-C(10)	112.1(3)	C(12')-C(11')-C(10')	110.9(3)
C(14)-C(11)-C(10)	109.0(3)	C(14')-C(11')-C(10')	109.7(3)
O(1)-C(12)-O(2)	119.5(4)	O(1')-C(12')-O(2')	119.7(4)
O(1)-C(12)-C(11)	128.9(4)	O(1')-C(12')-C(11')	130.1(4)
O(2)-C(12)-C(11)	111.6(4)	O(2')-C(12')-C(11')	110.1(4)
O(3)-C(13)-O(2)	120.0(4)	O(3')-C(13')-O(2')	119.9(4)

O(3)-C(13)-C(14)	129.8(4)	O(3')-C(13')-C(14')	129.8(4)
O(2)-C(13)-C(14)	110.2(4)	O(2')-C(13')-C(14')	110.3(4)
C(13)-C(14)-C(11)	104.1(3)	C(13')-C(14')-C(11')	104.3(3)
C(13)-C(14)-C(15)	112.4(3)	C(13')-C(14')-C(15')	111.1(3)
C(11)-C(14)-C(15)	109.4(3)	C(11')-C(14')-C(15')	109.6(3)
C(17)-C(15)-C(16)	110.4(3)	C(17')-C(15')-C(16')	110.7(3)
C(17)-C(15)-C(14)	106.4(3)	C(17')-C(15')-C(14')	105.9(3)
C(16)-C(15)-C(14)	104.7(3)	C(16')-C(15')-C(14')	104.6(3)
C(8)-C(16)-C(9)	60.1(2)	C(8')-C(16')-C(9')	60.1(3)
C(8)-C(16)-C(15)	121.9(3)	C(8')-C(16')-C(15')	120.7(3)
C(9)-C(16)-C(15)	110.5(3)	C(9')-C(16')-C(15')	110.8(3)
C(18)-C(17)-C(15)	114.7(4)	C(18')-C(17')-C(15')	115.0(3)
C(17)-C(18)-C(10)	115.0(4)	C(17')-C(18')-C(10')	114.4(4)
Dihedral angles (°)		Dihedral angles (°)	
α [b)]	29.4	α' [b)]	28.6
β [b)]	14.3	β' [b)]	13.7

a) The unit cell (Z = 8) contains two independent molecules, **4a** and **4a'**, in the ratio 1:1.

b) The dihedral angles α = C(1,2,7)/C(2,3,6,7) and β = C(2,3,6,7)/C(3,4,5,6); α' = C(1',2',7')/C(2',3',6',7') and β' = C(2',3',6',7')/C(3',4',5',6') define the bending of the cyclohepta-2,4,6-trienyl ring (cf. Fig. 2).

The diffraction data and the refinement parameters for **4a**, calculated from the X-ray structure analysis, are shown in Table 8.

Table 8. Crystal data and structure refinement for 4a

Empirical formula	$C_{18}H_{16}O_3S$	
Formula weight	312.38	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 10.6313(13) Å	α = 90°
	b = 22.487(2) Å	β = 95.212(7)°
	c = 12.6805(12) Å	γ = 90°
Volume	3019.0(5) $Å^3$	
Z	8	
Density (calculated)	1.383 Mg/m^3	
Absorption coefficient	0.225 mm^{-1}	
F(000)	1328	
Crystal size	0.18 x 0.15 x 0.12 mm^3	
θ range for data collection	1.85 to 24.99°	
Index ranges	-12<h<1, -26<k<1, -15<l<15	
Reflections collected	5564	
Independent reflections	4328 [R(int) = 0.0255]	
Completeness to θ = 24.99°	81.3 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4328 / 0 / 398	
Goodness-of-fit on F^2	0.986	
Final R indices [I > 2σ (I)]	R1 = 0.0564, wR2 = 0.1537	
R indices (all data)	R1 = 0.0877, wR2 = 0.1769	
Extinction coefficient	0.0027(10)	
Largest diff. peak and hole	0.442 and -0.548 $e \cdot Å^{-3}$	

2.3 Diels-Alder Reactions of $(C_7H_7)_2$

Diels-Alder reactions were carried out with ditropyl, $(C_7H_7)_2$ (**3**), in THF solution under reflux in the presence of maleic anhydride, maleimide or N-phenyl maleimide (Fig. 8). Compounds **5a**, **5b** and **5c** were obtained, respectively, which were isolated as white powders.

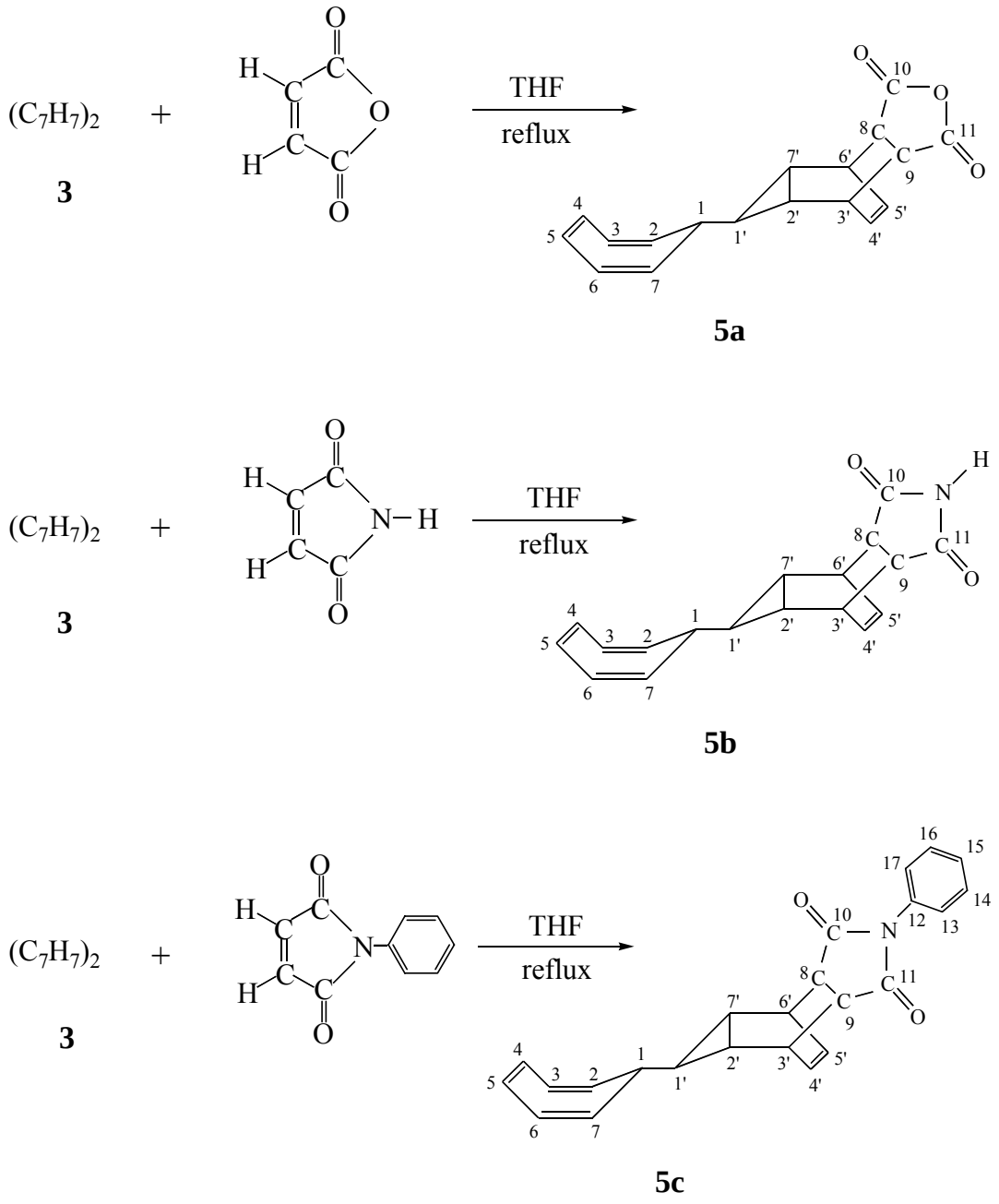


Fig.8. Synthesis of the Diels-Alder adducts **5a**, **5b** and **5c**

NMR-Spectroscopic Characterization

From the ^{1}H NMR and ^{13}C NMR spectra of the products **5a**, **5b** and **5c**, it is indicated that a similar Diels-Alder reaction takes place when ditropyl, $(C_7H_7)_2$ (**3**), reacts with maleic anhydride, maleimide and N-phenyl maleimide (Table 9). The spectra of the products **5a**, **5b** and **5c** are very similar with that of the products **4a**, **4b** and **4c** respectively. The products contain only one cycloheptatrienyl ring which has reacted, whereas the other ring is unchanged. For the unreacted cycloheptatrienyl ring, chemical shifts of the protons show a variation, especially for the proton 1, compared with those at the corresponding positions of ditropyl (**3**). The substituted ring has changed to the norcaradienyl isomer with a triangle. This is evident in particular from the high-field shift of the signals assigned to the "aliphatic" positions $H^{1'}$, $H^{2'}$ and $H^{7'}$. The protons of $H^{3'}$, $H^{6'}$ and H^8, H^9 also shift to higher magnetic field because new bonds were formed between the carbons of $C^{3'}$, $C^{6'}$ and C^8, C^9. In addition, the chemical shifts of $H^{4'}$and $H^{5'}$ also changed to higher magnetic field due to the disappearance of the double bonds between $C^{2'}$, $C^{3'}$ and $C^{6'}$, $C^{7'}$.

Table 9. NMR data of the Diels-Alder adducts 5a, 5b and 5c (cf. Fig. 8) [a), b)]

	5a	**5b**	**5c**
^{1}H-NMR			
$\delta(H^1)$	3.54t (1H)	3.40s (1H)	3.55s (1H)
$\delta(H^2, H^7)$	5.18m (2H)	5.13m (2H)	5.26m (2H)
$\delta(H^3, H^6)$	6.13dt (2H)	6.05dt (2H)	6.11dt (2H)
$\delta(H^4, H^5)$	6.59t (2H)	6.53t (2H)	6.59t (2H)
$\delta(H^{1'})$	3.54t (1H)	3.40s (1H)	3.55s (1H)
$\delta(H^{2'}, H^{7'})$	1.02s (2H)	0.97s (2H)	1.04s (2H)
$\delta(H^{3'}, H^{6'})$	1.02s (2H)	0.97s (2H)	1.04s (2H)
$\delta(H^{4'}, H^{5'})$	5.98m (2H)	5.85m (2H)	5.95m (2H)
$\delta(H^8, H^9)$	3.20t (2H)	2.97t (2H)	3.08t (2H)
δ(NH)		8.85s (1H)	
δ(NPh)			7.34, 7.16 (5H)

^{13}C-NMR			
$\delta(C^1)$	40.8	40.8	40.9
$\delta(C^2, C^7)$	124.9	124.6	124.6
$\delta(C^3, C^6)$	125.3	125.5	125.6
$\delta(C^4, C^5)$	130.9	130.7	130.8
$\delta(C^{1'})$	22.1	21.7	21.5
$\delta(C^{2'}, C^{7'})$	15.9	16.1	16.3
$\delta(C^{3'}, C^{6'})$	33.5	33.2	33.7
$\delta(C^{4'}, C^{5'})$	129.4	128.5	128.7
$\delta(C^8, C^9)$	45.6	46.3	45.0
$\delta(C^{10}, C^{11})$	178.5	179.6	177.4
$\delta(C^{12})$			130.9
$\delta(C^{13}, C^{17})$			129.0
$\delta(C^{14}, C^{16})$			124.9
$\delta(C^{15})$			125.6

a) NMR data in $CDCl_3$ at 25 °C.

b) NMR Multiplicities: s singlet, d doublet, dt doublet of triplets, t triplet, m multiplet.

Chapter 3
Coordination Compounds Derived from Di(1-cyclohepta-2,4,6-trienyl) thioether, $S(C_7H_7)_2$

3.1 Carbonylchromium Complexes

Synthesis

Hexacarbonyl chromium, $Cr(CO)_6$, undergoes photo-decarbonylation in THF solution to generate the fragment $[Cr(CO)_5]$ which is stabilized in the solution by the donor solvent tetrahydrofuran. In the subsequent dark reaction, the thf ligand may be

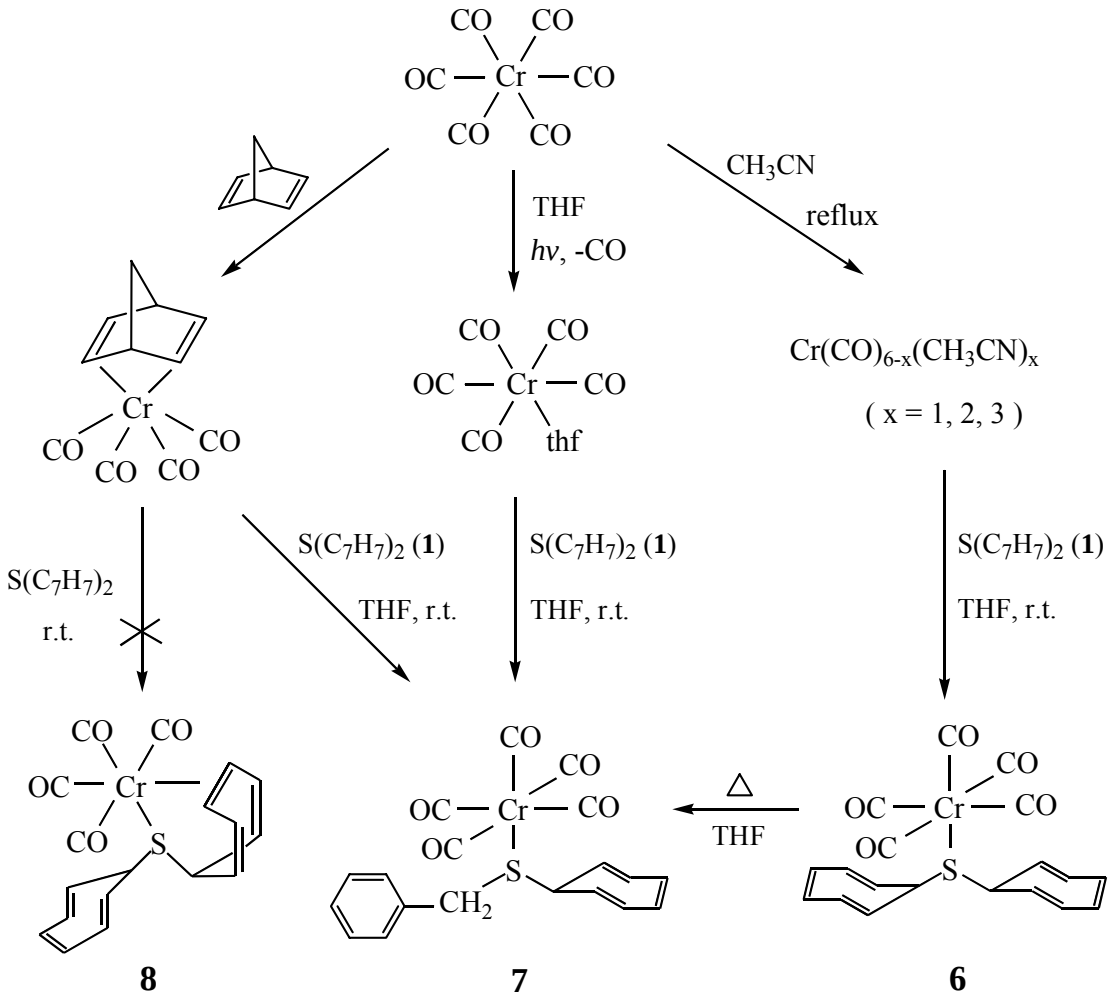
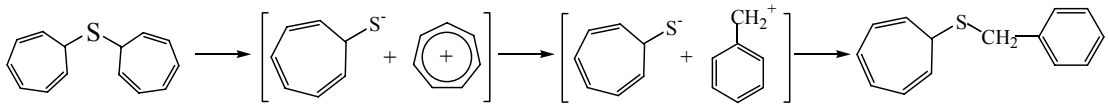


Fig.9. Synthesis of the complexes $Cr(CO)_5[S(C_7H_7)_2]$ (**6**) and $Cr(CO)_5[PhCH_2S(C_7H_7)]$ (**7**)

displaced by di(1-cyclohepta-2,4,6-trienyl) thioether, $S(C_7H_7)_2$ (**1**), to give the monosubstituted derivative $Cr(CO)_5[PhCH_2S(C_7H_7)]$ (**7**). X-ray analysis reveals that one seven-membered ring has remained unchanged while the other seven-membered ring has isomerized to a benzyl group. Considering the rich literature on the rearrangement between tropilidene and toluene, it is not surprising that, during the reaction, one seven-membered ring rearranges, probably through a tropylium cation which evolved from the unstable ditropyl thioether, *i.e.*



When using $Cr(CO)_4(\eta^4\text{-}C_7H_8)$ as the starting material [99], we expected to obtain the complex $Cr(CO)_4[(\eta^2\text{-}C_7H_7)S(C_7H_7)]$ (**8**). However, again complex **7** was isolated. Finally, from the reaction of a mixture of $Cr(CO)_{6-x}(CH_3CN)_x$ (x = 1, 2, 3) [100] and **1**, the complex $Cr(CO)_5[S(C_7H_7)_2]$ (**6**) could be obtained, in which two cycloheptatrienyl rings are freely pending (Fig. 9). Complex **6** could be converted to the complex **7** when it was heated in THF solution at 60 °C.

IR and NMR Spectroscopy

Table 10 contains the IR stretching frequencies of the carbonyl ligands (in pentane solution) and the ^1H and ^{13}C NMR data (in $CDCl_3$ solution) for the pentacarbonyl complexes **6** and **7**.

Table 10. NMR Spectroscopic data of the pentacarbonyl chromium complexes[a), b)]

	$Cr(CO)_5[S(C_7H_7)_2]$ **6**	$Cr(CO)_5[PhCH_2S(C_7H_7)]$ **7**
^1H-NMR		
$\delta(H^1)$	3.89t (2H)	4.16t (1H)
$\delta(H^2, H^7)$	5.52dd (4H)	5.69dd (2H)
$\delta(H^3, H^6)$	6.38m (4H)	6.43m (2H)
$\delta(H^4, H^5)$	6.68s (4H)	6.71dd (2H)
$\delta(CH_2)$		3.88s (2H)
$\delta(Ph)$		7.18-7.30 m (5H)

^{13}C-NMR		
$\delta(C^1)$	47.6	51.0
$\delta(C^2, C^7)$	121.3	121.6
$\delta(C^3, C^6)$	128.7	129.5
$\delta(C^4, C^5)$	132.0	132.0
$\delta(CH_2)$		43.3
δ(Ph)		128.2(p), 128.7(m), 129.6(o), 134.6(i)
δ(CO) (cis)	215.2	214.9
δ(CO) (trans)	221.3	221.3
IR: ν(CO) (cm^{-1}) (pentane)	2075(w), 1951(s), 1941(m), 1928(m)	2068(w), 1945(s), 1939(s), 1930(m)

a) NMR Data in $CDCl_3$ at 25 °C.

b) NMR Multiplicities: s singlet, dd doublet of doublets, t triplet, m multiplet.

The complexes **6** and **7** consistently show two ^{13}C NMR signals for the 5 CO ligands, the stronger peak corresponding to the 4 CO ligands *cis* to the sulfane ligand appears at higher field, cf. $Cr(CO)_6$ 213.9 ppm. The absorptions of complex **7** are similar to those of $Cr(CO)_5[S(C_2H_5)CH_2Ph]$ (2068m, 1986w, 1941vs, 1933sh) in hexane [101], which indicates comparable octahedral structures.

The ^{1}H and ^{13}C NMR spectra are simple, as long as the sulfane ligand, $S(C_7H_7)_2$, carries two unchanged and uncoordinated 1-cyclohepta-2,4,6-trienyl rings which give rise to 4 signals (as in complex **6**). For complex **7**, a total of nine ^{13}C NMR signals are observed, *i.e.* 4 originating from the free seven-membered ring and 5 from the benzyl group.

In the ^{1}H NMR spectra of **6** and **7**, a multiplet is generally observed for the protons H^3/H^6 of the uncoordinated cyclohepta-2,4,6-trienyl substituents; the shift difference ($\Delta\delta$) is about 0.2 ppm down-field, compared with the free sulfane **1**. The benzyl group in complex **7** has similar ^{1}H chemical shifts as that in $Cr(CO)_5[S(C_2H_5)CH_2Ph]$ ($\delta(CH_2)$ 3.82, δ(Ph) 7.34) [101]. The electron loss as a result of coordination is clearly shown and even reflected in the downfield shift for the benzyl CH_2 singlet of the coordinated $[S(C_7H_7)CH_2Ph]$ sulfane ligand ($\delta(CH_2)$ 3.88), as compared with the free ligand $S(CH_2Ph)_2$ ($\delta(CH_2)$ 3.59) [102]. Fig. 10 shows a typical ^{13}C NMR spectrum of complex **7**, in which the signals are sharp and do not show resolved coupling.

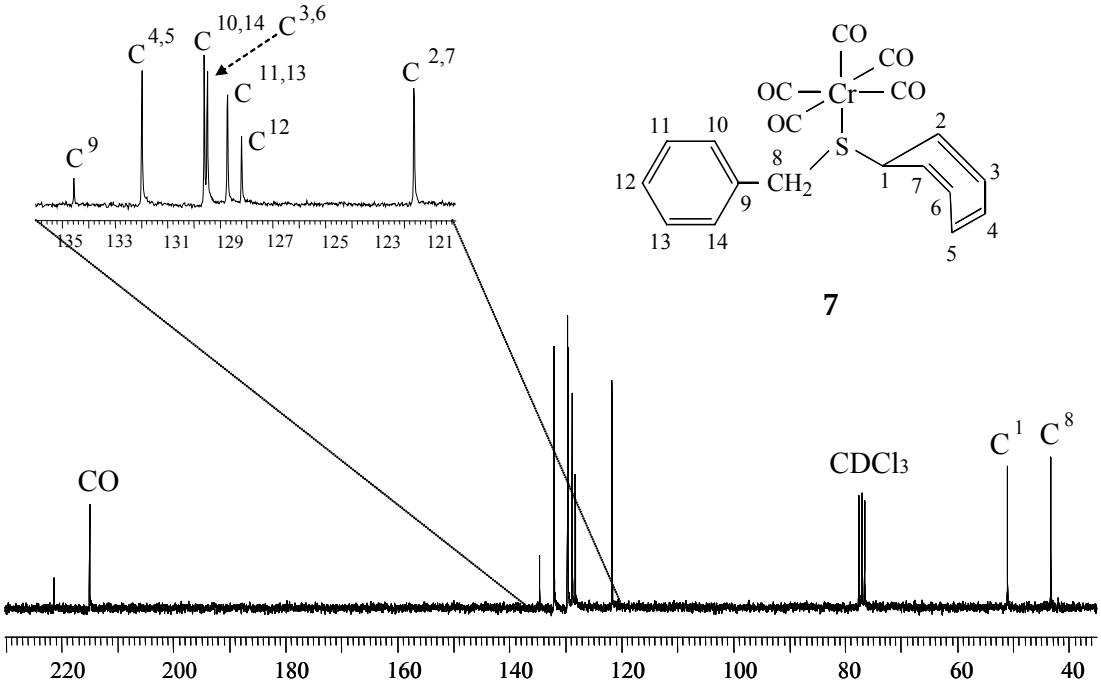


Fig.10. ^{13}C NMR Spectrum of $Cr(CO)_5[PhCH_2S(C_7H_7)]$ (**7**) (in $CDCl_3$ at 25 °C)

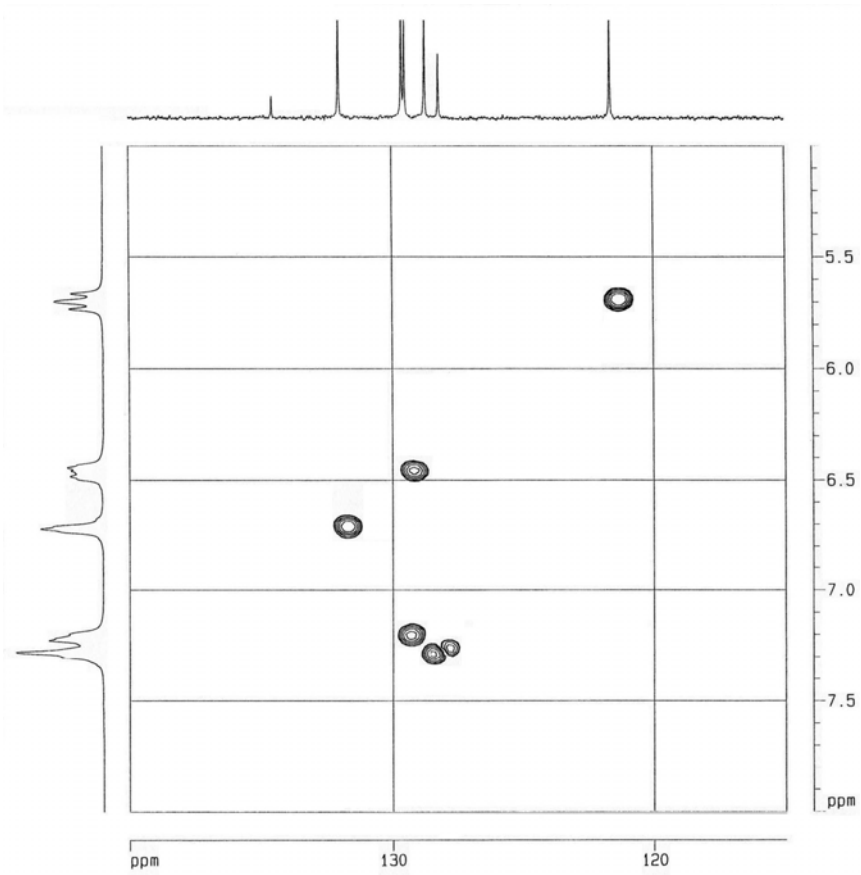


Fig.11. Contour plot of the 2D $^{13}C/^{1}H$ HETCOR NMR experiment with complex **7** (in $CDCl_3$ at 25 °C)

The 2D $^{13}C/^{1}H$ HETCOR experiment (Fig. 11) confirms the mutual assignment of ^{1}H and ^{13}C NMR signals. In the phenyl group the chemical shift of C(9) is 134.6 ppm; the ortho-carbons (C(10) and C(11)) are observed at 129.6 ppm; the meta-carbons (C(11) and C(13)) at 128.7 ppm and the para-carbon (C(12)) at 128.2 ppm. In addition, the signal of C(8) appears at 43.3 ppm, slightly downfield as compared with the free thioether $S(CH_2Ph)_2$ ($\delta(CH_2)$ 35.6) [102].

Molecular Structure of $Cr(CO)_5[PhCH_2S(C_7H_7)]$ (7)

The relevant distances and angles of the inner sphere around the central metal Cr are compiled for complex **7** in Table 11. The numbering system is given in Fig. 12.

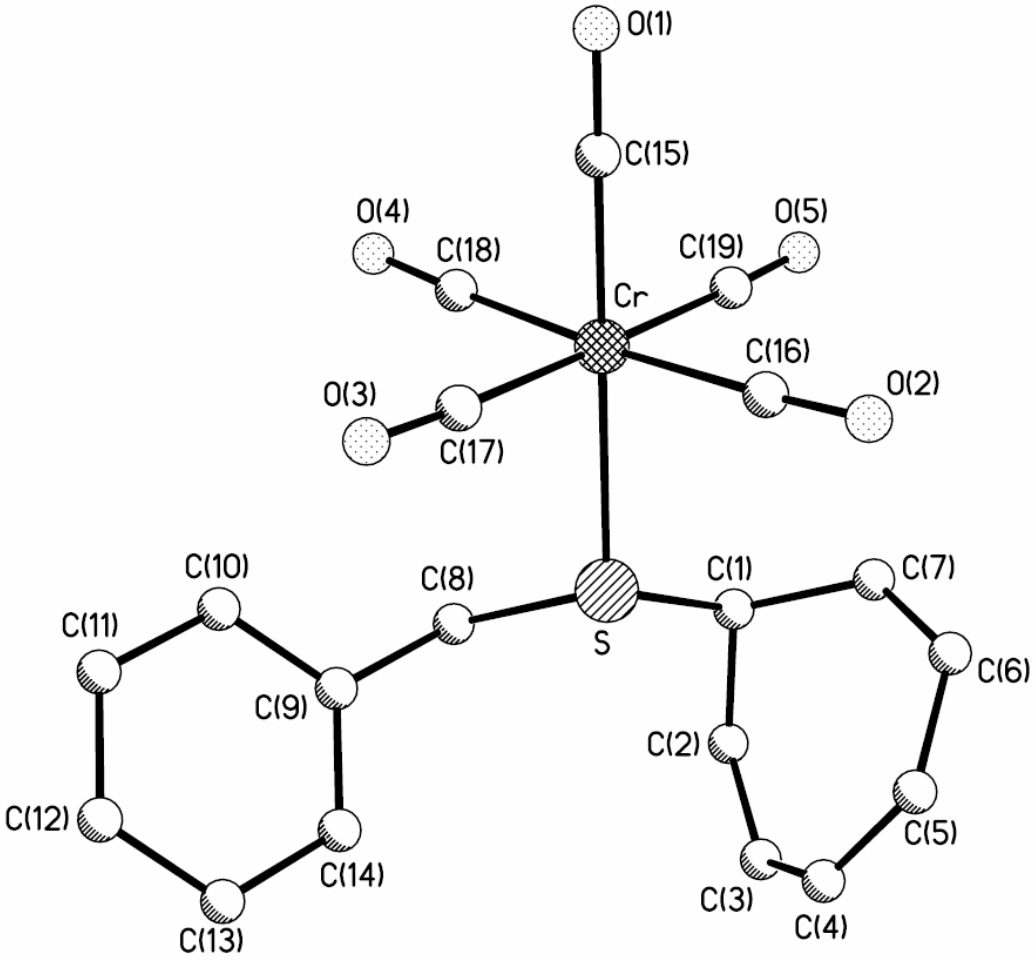


Fig.12. Structure of $Cr(CO)_5[PhCH_2S(C_7H_7)]$ (**7**)

Table 11. Relevant distances and angles of complex 7

Distances (pm)		Angles (°)	
Cr-C(15)	184.0(7)	C(15)-Cr-C(18)	87.5(3)
Cr-C(18)	188.4(7)	C(15)-Cr-C(16)	89.2(3)
Cr-C(16)	189.6(7)	C(18)-Cr-C(16)	176.3(3)
Cr-C(17)	189.3(7)	C(15)-Cr-C(17)	89.0(3)
Cr-C(19)	190.6(7)	C(18)-Cr-C(17)	90.9(3)
		C(16)-Cr-C(17)	90.6(3)
Cr-S	242.68(16)	C(15)-Cr-C(19)	90.4(3)
		C(18)-Cr-C(19)	88.5(3)
S-C(8)	183.1(6)	C(16)-Cr-C(19)	89.9(3)
S-C(1)	186.3(5)	C(17)-Cr-C(19)	179.2(3)
		C(15)-Cr-S	175.5(2)
O(1)-C(15)	116.7(7)	C(18)-Cr-S	95.6(2)
O(2)-C(16)	112.9(7)	C(16)-Cr-S	87.84(19)
O(3)-C(17)	113.9(7)	C(17)-Cr-S	87.6(2)
O(4)-C(18)	115.0(7)	C(19)-Cr-S	93.0(2)
O(5)-C(19)	113.1(7)	C(8)-S-C(1)	98.4(3)
		C(8)-S-Cr	111.2(2)
C(1)-C(7)	146.8(9)	C(1)-S-Cr	112.8(2)
C(1)-C(2)	147.7(9)	C(7)-C(1)-C(2)	110.0(6)
C(2)-C(3)	132.6(12)	C(7)-C(1)-S	110.0(4)
C(3)-C(4)	137.1(16)	C(2)-C(1)-S	111.1(4)
C(4)-C(5)	134.9(17)	C(3)-C(2)-C(1)	123.9(8)
C(5)-C(6)	145.8(16)	C(2)-C(3)-C(4)	127.5(10)
C(6)-C(7)	128.4(11)	C(5)-C(4)-C(3)	128.5(12)
C(8)-C(9)	150.6(7)	C(4)-C(5)-C(6)	121.6(11)
C(9)-C(14)	136.5(8)	C(7)-C(6)-C(5)	128.5(9)
C(9)-C(10)	137.6(8)	C(6)-C(7)-C(1)	125.5(7)
C(10)-C(11)	138.8(9)	C(9)-C(8)-S	110.2(4)
C(11)-C(12)	136.0(10)	C(14)-C(9)-C(10)	119.2(6)
C(12)-C(13)	136.5(10)	C(14)-C(9)-C(8)	120.4(5)
C(13)-C(14)	138.8(9)	C(10)-C(9)-C(8)	120.4(6)
		C(9)-C(10)-C(11)	119.9(6)
		C(12)-C(11)-C(10)	119.9(7)

		C(11)-C(12)-C(13)	121.1(7)
		C(12)-C(13)-C(14)	118.6(7)
		C(9)-C(14)-C(13)	121.3(7)
		O(1)-C(15)-Cr	178.4(6)
		O(2)-C(16)-Cr	176.1(6)
		O(3)-C(17)-Cr	176.7(6)
		O(4)-C(18)-Cr	177.5(6)
		O(5)-C(19)-Cr	177.7(6)

In the crystal lattice of complex $Cr(CO)_5[PhCH_2S(C_7H_7)]$ (**7**), the chromium atom, surrounded by five carbonyl groups and one sulfur atom, assumes an approximate octahedral environment. One cycloheptatrienyl substituent (containing C(1)) is freely pending. On the contrary, the other ring substituent has changed to a benzyl group where C(8) is coplanar with the phenyl ring plane. The angles Cr-S-C(1) (112.8(2)°) and Cr-S-C(8) (111.2(2)°) in **7** are very similar to the corresponding angles (112.0(3)° and 106.0(3)°) in the complex $Cr(CO)_5[PhCH_2S(C_2H_5)]$ [101]. The angle C(8)-S-C(1) is 98.4(3)°, which is slightly smaller than the corresponding angle in the free sulfane **1** (100.71(12)°) due to the coordination of the sulfur atom to the metal. The bond length of S-C(1) (186.3(5) pm) in complex **7** is a little longer than the bond length of S-C(1) (184.43(18) pm) in the free sulfane **1**. The CO ligand *trans* to sulfur is slightly closer to the metal (Cr-C(15) 184.0(7) pm) than the other four carbonyl groups (Cr-C(16) 189.6(7) pm, Cr-C(17) 189.3(7) pm, Cr-C(18) 188.4(7) pm, Cr-C(19) 190.6(7) pm), and is slightly less bent (angle S-Cr-C(15) 175.5(2)°). Nevertheless, the *trans* C-O distance (116.7(7) pm) is markedly longer than the mean value of the 4 *cis* C-O distances (113.7(7) pm). The four *cis* carbonyl groups are nearly coplanar and the average Cr-C bond length is 189.5(7) pm, which is slightly longer than the average *cis* Cr-C bond length (187.9 pm) in $Cr(CO)_5[PhCH_2S(C_2H_5)]$ [101] and slightly shorter than the Cr-C distance (190.9 pm) in $Cr(CO)_6$ [103]. The dihedral angle between the plane C(16)-Cr-C(17) and the plane C(18)-Cr-C(19) is 3.4°. The chromium-sulfur bond distance (242.68(16) pm) is slightly shorter than the Cr-S bond length in (^{t}BuSH)$Cr(CO)_5$ (243.9(2) pm) [104] and in $Cr(CO)_5[PhCH_2S(C_2H_5)]$ (245.9(2) pm) [101], but significantly shorter than the Cr-S bond length (251.0(2) pm) in $Cr(CO)_5[SP(CH_3)_3]$ [105], indicating a smaller σ(donor)/π(acceptor) ratio for $PhCH_2S(C_7H_7)$ as compared with $PhCH_2S(C_2H_5)$ and with the ligand, $(CH_3)_3PS$, for which practically no π interaction has been assumed [105].

The diffraction data and the refinement parameters for complex **7**, calculated from the X-ray structure analysis, are shown in Table 12.

Table 12. Crystal data and structure refinement for complex 7

Empirical formula	$C_{18}\ H_{14}\ Cr\ O_4\ S$
Formula weight	378.35
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*C*2/c
Unit cell dimensions	a = 18.8566(15) Å α = 90°
	b = 16.3879(12) Å β = 121.061(5)°
	c = 14.5906(11) Å γ = 90°
Volume	3862.3(5) $Å^3$
Z	8
Density (calculated)	1.301 Mg/m^3
Absorption coefficient	0.716 mm^{-1}
F(000)	1552
Crystal size	0.18 x 0.15 x 0.12 mm^3
θ range for data collection	2.49 to 25.00°
Index ranges	-1<h<22, -1<k<19, -17<l<15
Reflections collected	3949
Independent reflections	3342 [R(int) = 0.0366]
Completeness to θ = 25.00°	98.6 %
Absorption correction	Empirical
Max. and min. transmission	0.5917 and 0.5266
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3342 / 0 / 235
Goodness-of-fit on F^2	0.963
Final R indices [I > 2σ (I)]	R1 = 0.0594, wR2 = 0.1382
R indices (all data)	R1 = 0.1187, wR2 = 0.1745
Largest diff. peak and hole	0.421 and -0.314 e·$Å^{-3}$

3.2 Carbonylmolybdenum Complexes

Synthesis

The same methods which were used for the chromium complexes were also applied for the synthesis of new molybdenum complexes. Thus, hexacarbonyl molybdenum, $Mo(CO)_6$, was irradiated in THF solution with the goal to generate $Mo(CO)_5$(thf). In the subsequent dark reaction, we expected that the thf ligand might be displaced by di(1-cyclohepta-2,4,6-trienyl) thioether, $S(C_7H_7)_2$ (**1**), to give the monosubstituted derivative **9**, in which two seven-membered rings are freely pending. However, the tetracarbonyl molybdenum complex $Mo(CO)_4[(\eta^2\text{-}C_7H_7)S(C_7H_7)]$ (**10**)

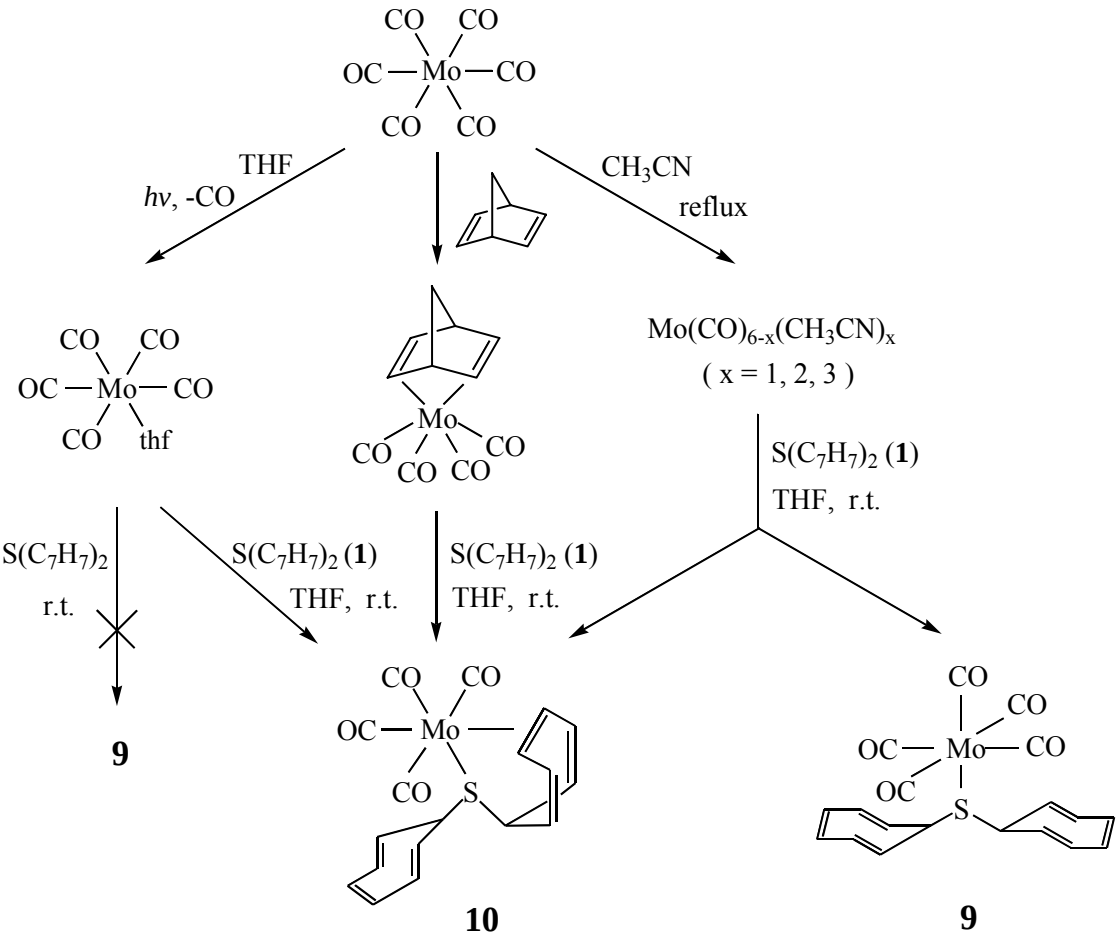


Fig.13. Synthesis of the complexes $Mo(CO)_5[S(C_7H_7)_2]$ (**9**) and $Mo(CO)_4[(\eta^2\text{-}C_7H_7)S(C_7H_7)]$ (**10**)

was obtained, in which the ligand, $S(C_7H_7)_2$, is coordinated to the metal through a lone pair of electrons at the sulfur atom and the central C=C double bond of one

cyclohepta-2,4,6-trienyl substituent. In addition, when $Mo(CO)_4(\eta^4\text{-}C_7H_8)$ [99] was used as the starting material, the complex **10** was also obtained. Surprisingly, the complex $Mo(CO)_5[S(C_7H_7)_2]$ (**9**) could be obtained from the reaction of the acetonitrile complexes [100], $Mo(CO)_{6-x}(CH_3CN)_x$ (x = 1, 2, 3), in THF solution. The sulfane, $S(C_7H_7)_2$, behaves as a two-electron ligand in **9**, being coordinated to molybdenum exclusively through a lone pair of electrons at the sulfur atom (Fig. 13).

We also tried to prepare the complex $Mo(CO)_3[(\eta^6\text{-}C_7H_7)S(C_7H_7)]$ (**11**), in which only one seven-membered ring would be coordinated to the metal. But when hexacarbonyl molybdenum was heated with the sulfane **1**, the ligand lost its sulfur and the ditropyl complex $Mo(CO)_3[(\eta^6\text{-}C_7H_7)(C_7H_7)]$ (**12**) (*endo*-hydrogen isomer **12a** and *exo*-hydrogen isomer **12b**) was obtained. Complex **12a** had already been reported in the literature [106], but had been prepared directly from hexacarbonyl molybdenum and ditropyl.

In another attempt towards the synthesis of **11**, (η^6-mesitylene)tricarbonyl molybdenum, $(\eta^6\text{-}C_6H_3Me_3)Mo(CO)_3$, was first prepared [107] and then reacted with the sulfane **1**. The expectation was that the mesitylene might be displaced by **1**. However, instead of complex **11**, the ditropyl complex **12** (isomers **12a** and **12b**) was again obtained (Fig. 14).

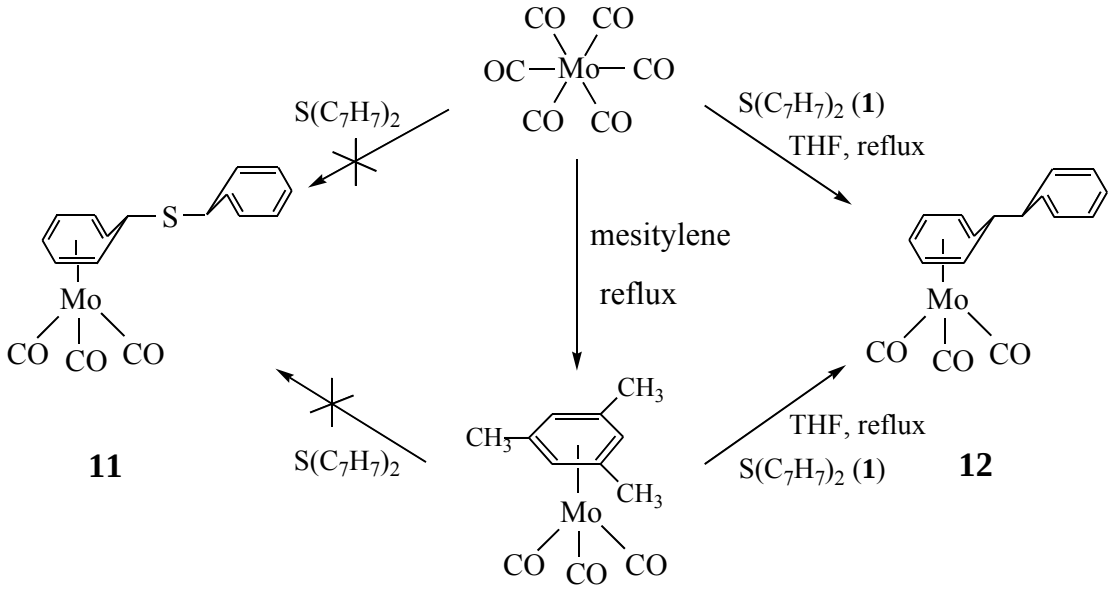


Fig.14. Synthesis of the complex $Mo(CO)_3[(\eta^6\text{-}C_7H_7)(C_7H_7)]$ (**12**)

It might be concluded from these reactions, that di(1-cyclohepta-2,4,6-trienyl) thioether (**1**) tends to lose its sulfur when reacted with metal complexes to give ditropyl complexes.

IR and NMR Spectroscopy

Table 13 contains the IR stretching frequencies of the carbonyl ligands (in pentane solution) and the ^1H and ^{13}C NMR data (in $CDCl_3$ solution).

Table 13. NMR Spectroscopic data of the molybdenum complexes [a), b)]

	$Mo(CO)_5[S(C_7H_7)_2]$ **9**	$Mo(CO)_4[(\eta^2\text{-}C_7H_7)S(C_7H_7)]$ **10**	$Mo(CO)_3[(\eta^6\text{-}C_7H_7)(C_7H_7)]$ **12**	
^1H-NMR			**12a** [106]	**12b**
$\delta(H^1)$	3.92t (2H)	3.89t [7.9] (1H)	0.79m (1H)	2.07m (1H)
$\delta(H^2, H^7)$	5.55m (4H)	5.60m (2H)	5.04m (2H)	5.16m (2H)
$\delta(H^3, H^6)$	6.38m (4H)	6.47m (2H)	6.11m (2H)	6.25m (2H)
$\delta(H^4, H^5)$	6.70t (4H)	6.67m (2H)	6.53t (2H)	6.70t (2H)
$\delta(H^{1'})$		4.82t [8.1] (1H)	3.27m (1H)	2.42m (1H)
$\delta(H^{2'}, H^{7'})$		5.60m (2H)	3.98t (2H)	3.41t (2H)
$\delta(H^{3'}, H^{6'})$		6.62m (2H)	4.92m (2H)	4.97m (2H)
$\delta(H^{4'}, H^{5'})$		5.60m (2H)	5.92m (2H)	6.01m (2H)
^{13}C-NMR				
$\delta(C^1)$	48.0	42.6	49.1	43.0
$\delta(C^2, C^7)$	121.9	125.3	122.4	123.3
$\delta(C^3, C^6)$	128.6	130.3	126.3	126.2
$\delta(C^4, C^5)$	131.8	131.8	130.7	131.2
$\delta(C^{1'})$		47.3	39.9	39.4
$\delta(C^{2'}, C^{7'})$		124.5	68.1	62.6
$\delta(C^{3'}, C^{6'})$		129.7	100.7	100.3
$\delta(C^{4'}, C^{5'})$		84.6	97.0	97.4
δ(CO)	204.7 (cis) 211.5 (trans)	213.8, 213.5		
IR: ν(CO) (cm^{-1}) [c)] (pentane)	2075(w),1954(s), 1945(s), 1933(s)	2034(m), 1945(s), 1931(s), 1898(s)	1997(s), 1934(s), 1910(s)	

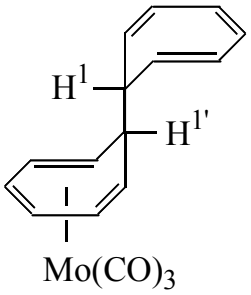
a) NMR Data in $CDCl_3$ at 25 °C.

b) NMR Multiplicities: s singlet, d doublet, dt doublet of triplets, t triplet, m multiplet.

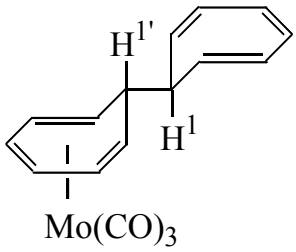
c) For comparison: $Mo(CO)_6$, ν(CO) in pentane 1990 cm^{-1}.

The number of 4 ν(CO) bands observed for the complex **10** is in agreement with the number of CO ligands. The $Mo(CO)_3$ unit in complex **12** gives rise to a typical tricarbonylmetal pattern with 3 absorptions.

The ^1H and ^{13}C NMR spectra of complex **9** are simple because the sulfane ligand, $S(C_7H_7)_2$, carries two uncoordinated cyclohepta-2,4,6-trienyl rings which give rise to four signals. A multiplet is observed for the protons H^2/H^7 and H^3/H^6 of the cyclohepta-2,4,6-trienyl substituents; the shift difference (Δδ) of H^1 is about 0.3 ppm down-field compared with the free sulfane **1**. The complex **9** shows two ^{13}C NMR signals for the 5 CO ligands, the stronger peak (corresponding to the 4 CO ligands *cis* to the sulfane ligand) appears at higher field (cf. $Mo(CO)_6$ 201.0). For the chelate complex **10**, a total of ten ^{13}C NMR signals are observed, (*i.e.* 4 originating from the free seven-membered ring, 4 from the η^2-coordinated cyclohepta-2,4,6-trienyl ring and 2 from the CO ligands). The signals of the coordinated double bond ($H^{4',5'}$ and $C^{4',5'}$) are shifted upfield ($\delta(H^{4',5'})$ 5.60, $\delta(C^{4',5'})$ 84.6) compared to the uncoordinated sulfane **1** ($\delta(H^{4,5})$ 6.58, $\delta(C^{4,5})$ 131.2).



12a



12b

When hexacarbonyl molybdenum reacted with the sulfane **1**, the ligand decomposed and $Mo(CO)_3[(\eta^6\text{-}C_7H_7)(C_7H_7)]$ (**12**) was obtained. The mixture containing both the *endo*-hydrogen isomer **12a** and the *exo*-hydrogen isomer **12b** could be separated through thin layer chromatography (TLC). The isolated yield was low owing to the formation of molybdenum sulfide. In addition, complex **12a** was isolated in a higher yield than complex **12b**. The signal of $H^{1'}$ in the coordinated cyclohepta-2,4,6-trienyl ring (**12a** $\delta(H^{1'})$ 3.27, **12b** $\delta(H^{1'})$ 2.42) is shifted down-field compared with ditropyl (**3**) ($\delta(H^1)$ 1.95). When the $H^{1'}$ hydrogen is *endo* to the metal, the adjacent CH signal ($H^{2'}$, $H^{7'}$) is expected at higher frequency than when $H^{1'}$ is *exo* to the metal. This is clearly the case when comparing the observed shifts for complex **12a** and **12b**.

Molecular Structure of $Mo(CO)_4[(\eta^2\text{-}C_7H_7)S(C_7H_7)]$ (10)

The molecular structure of the complex $Mo(CO)_4[(\eta^2\text{-}C_7H_7)S(C_7H_7)]$ (**10**) is presented in Fig. 15. Relevant distances and angles of the inner sphere around the central metal Mo are summarized in Table 14.

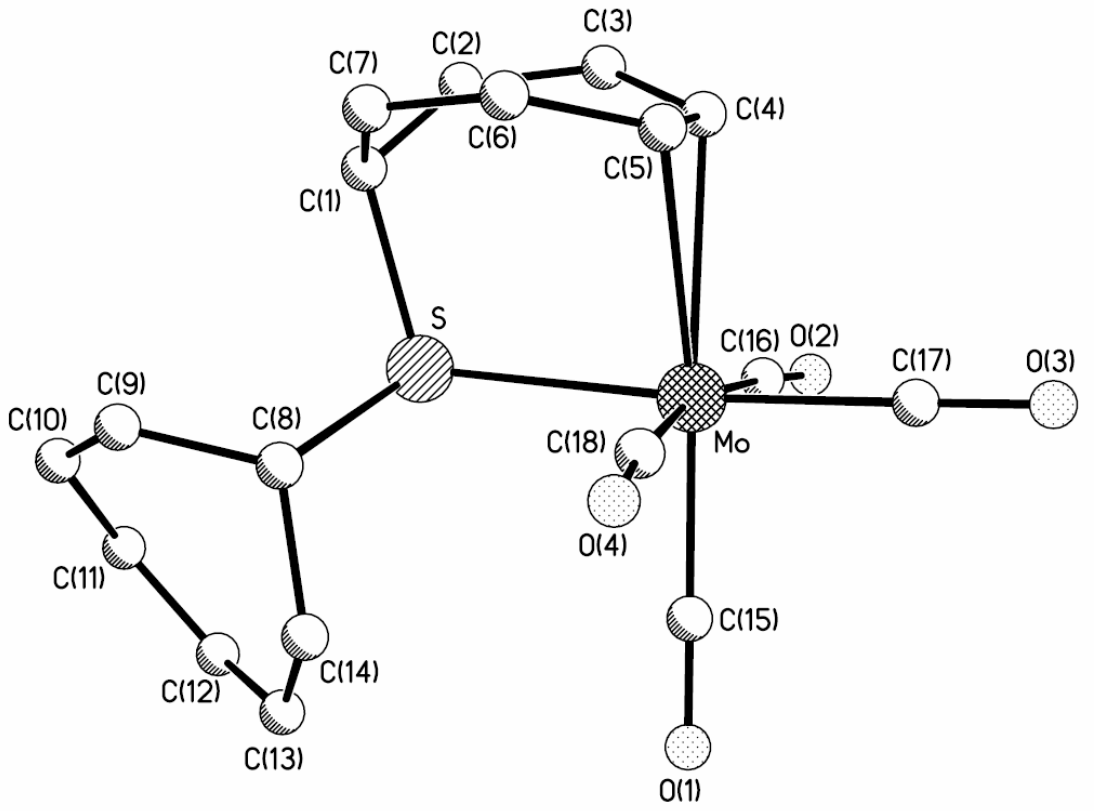


Fig.15. Structure of $Mo(CO)_4[(\eta^2\text{-}C_7H_7)S(C_7H_7)]$ (**10**)

Table 14. Relevant distances and angles of complex 10

Distances (pm)		Angles (°)	
Mo-C(17)	195.6(12)	C(17)-Mo-C(15)	91.2(5)
Mo-C(15)	196.1(13)	C(17)-Mo-C(18)	87.9(4)
Mo-C(18)	201.6(13)	C(15)-Mo-C(18)	85.2(5)
Mo-C(16)	203.2(14)	C(17)-Mo-C(16)	85.0(4)
Mo-C(5)	248.6(10)	C(15)-Mo-C(16)	87.2(5)
Mo-C(4)	250.2(10)	C(18)-Mo-C(16)	169.4(5)
Mo-S	253.8(3)	C(17)-Mo-C(5)	90.7(4)
		C(15)-Mo-C(5)	162.2(5)

		C(18)-Mo-C(5)	77.2(4)
S-C(1)	186.2(10)	C(16)-Mo-C(5)	110.6(4)
S-C(8)	186.5(10)	C(17)-Mo-C(4)	90.5(4)
		C(15)-Mo-C(4)	165.3(5)
O(1)-C(15)	115.7(12)	C(18)-Mo-C(4)	109.5(4)
O(2)-C(16)	115.1(13)	C(16)-Mo-C(4)	78.4(4)
O(3)-C(17)	115.2(12)	C(5)-Mo-C(4)	32.3(4)
O(4)-C(18)	114.3(13)	C(17)-Mo-S	175.2(3)
		C(15)-Mo-S	93.1(3)
C(1)-C(7)	148.8(14)	C(18)-Mo-S	94.6(3)
C(1)-C(2)	149.0(15)	C(16)-Mo-S	93.1(3)
C(2)-C(3)	132.1(15)	C(5)-Mo-S	85.9(3)
C(3)-C(4)	143.5(15)	C(4)-Mo-S	84.8(3)
C(4)-C(5)	138.8(15)	C(1)-S-C(8)	99.6(5)
C(5)-C(6)	143.4(15)	C(1)-S-Mo	106.8(4)
C(6)-C(7)	133.4(15)	C(8)-S-Mo	109.1(3)
C(8)-C(14)	148.9(14)	C(7)-C(1)-C(2)	113.4(9)
C(8)-C(9)	149.5(16)	C(7)-C(1)-S	112.2(7)
C(9)-C(10)	126.0(18)	C(2)-C(1)-S	107.4(7)
C(10)-C(11)	145.0(2)	C(3)-C(2)-C(1)	124.0(11)
C(11)-C(12)	134.0(2)	C(2)-C(3)-C(4)	127.8(12)
C(12)-C(13)	143.0(19)	C(5)-C(4)-C(3)	123.8(12)
C(13)-C(14)	132.8(16)	C(5)-C(4)-Mo	73.2(6)
		C(3)-C(4)-Mo	114.7(7)
		C(4)-C(5)-C(6)	127.5(11)
		C(4)-C(5)-Mo	74.5(6)
		C(6)-C(5)-Mo	113.6(7)
		C(7)-C(6)-C(5)	126.5(11)
		C(6)-C(7)-C(1)	123.5(11)
		C(14)-C(8)-C(9)	109.7(9)
		C(14)-C(8)-S	108.5(8)
		C(9)-C(8)-S	111.1(8)
		C(10)-C(9)-C(8)	128.8(14)
		C(9)-C(10)-C(11)	125.9(14)
		C(12)-C(11)-C(10)	125.3(14)

		C(11)-C(12)-C(13)	126.9(15)
		C(14)-C(13)-C(12)	126.2(13)
		C(13)-C(14)-C(8)	125.9(11)
		O(1)-C(15)-Mo	179.1(12)
		O(2)-C(16)-Mo	173.7(12)
		O(3)-C(17)-Mo	179.1(11)
		O(4)-C(18)-Mo	174.7(11)

In the solid-state structure of the complex $Mo(CO)_4[(\eta^2\text{-}C_7H_7)S(C_7H_7)]$ (**10**), one cycloheptatrienyl substituent (containing C(8)) is uncoordinated. The other ring substituent (containing C(1)) approaches the coordination sphere of Mo via the olefinic double bond C(4)-C(5), and is therefore axially connected to the sulfur atom. The bond length C(4)-C(5) (138.8(15) pm) appears to be widened as a result of π-complexation. The angle Mo-S-C(1) (106.8(4)°) involving the axially connected ring substituent is smaller than the angle Mo-S-C(8) (109.1(3)°). The angle C(1)-S-C(8) (99.6(5)°) is slightly smaller than the corresponding angle in sulfane **1** (100.71(12)°). The bond lengths of S-C(1) and S-C(8) are 186.2(10) pm and 186.5(10) pm, respectively, which are longer than the corresponding bond length in sulfane **1** (184.43(18) pm). The CO ligand *trans* to sulfur is slightly closer to the metal (195.6(12) pm) than the other three carbonyl groups (Mo-C(15) 196.1(13) pm, Mo-C(16) 203.2(14) pm, Mo-C(18) 201.6(13) pm), and is slightly less bent (angle S-Mo-C(17) 175.2(3)°). The coordinated double bond, C(4)-C(5) (138.8(15) pm), is essentially coplanar with the 3 carbonyl carbon atoms C(15)C(16)C(18); the dihedral angle between the vector C(4)-C(5) and this plane is 1.2°. The central metal Mo is part of the plane C(4)C(5)MoC(15)O(1), whereas the two *cis*-carbonyl groups C(16)O(2) and C(18)O(4) are bent out (angle C(16)-Mo-C(18) 169.4(5)°). The bond distance of Mo-S (253.8(3) pm) is shorter than the corresponding bond length in $Mo(CO)_4[P(C_6H_5)_2(CH_2)_2SCH_3]$ (256.0(1) pm) and longer than the Mo-S bond to the positively charged sulfur atom in $Mo(CO)_4[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+$ (242.5(1) pm) [108].

The diffraction data and the refinement parameters for complex **10**, obtained from the X-ray structure analysis, are shown in Table 15.

Table 15. Crystal data and structure refinement for complex 10

Empirical formula	$C_{18}\,H_{14}\,Mo\,O_4\,S$
Formula weight	422.29
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 16.020(2) Å α = 90°
	b = 9.423(3) Å β = 102.011(9)°
	c = 11.955(2) Å γ = 90°
Volume	1765.2(6) $Å^3$
Z	4
Density (calculated)	1.589 Mg/m^3
Absorption coefficient	0.879 mm^{-1}
F(000)	848
Crystal size	0.15 x 0.14 x 0.04 mm^3
θ range for data collection	2.52 to 24.99°
Index ranges	-17<h<17, -1<k<11, -1<l<12
Reflections collected	3074
Independent reflections	2314 [R(int) = 0.0673]
Completeness to θ = 24.99°	74.6 %
Absorption correction	Empirical
Max. and min. transmission	0.3507 and 0.2716
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2314 / 0 / 217
Goodness-of-fit on F^2	0.998
Final R indices [I > 2σ (I)]	R1 = 0.0632, wR2 = 0.1296
R indices (all data)	R1 = 0.1253, wR2 = 0.1587
Largest diff. peak and hole	1.074 and -0.816 $e{\cdot}Å^{-3}$

3.3 Carbonyltungsten Complexes

Synthesis

Under the same reaction conditions as described for the carbonylchromium complexes, via a thf intermediate complex $W(CO)_5(thf)$, the pentacarbonyl tungsten complex $W(CO)_5[S(C_7H_7)_2]$ (**13**) was obtained, which can be converted to the benzyl complex $W(CO)_5[PhCH_2S(C_7H_7)]$ (**14**) when heated in THF solution at 50 °C. Complex **14** has the structure reported for the chromium complex **7**, *i.e.* one cyclohepta-2,4,6-trienyl substituent is rearranged to a benzyl group and the other seven-membered ring is unchanged. Complex **14** can also be obtained directly from $W(CO)_5(thf)$ and the sulfane (**1**). When the mixture of the acetonitrile tungsten complexes [100], $W(CO)_{6-x}(CH_3CN)_x$ (x = 1, 2, 3), was used as the starting material, the complexes $W(CO)_4[(\eta^2\text{-}C_7H_7)S(C_7H_7)]$ (**15**) and $W(CO)_5[S(C_7H_7)_2]$ (**13**) were obtained, and complex **15** was the main product (Fig. 16).

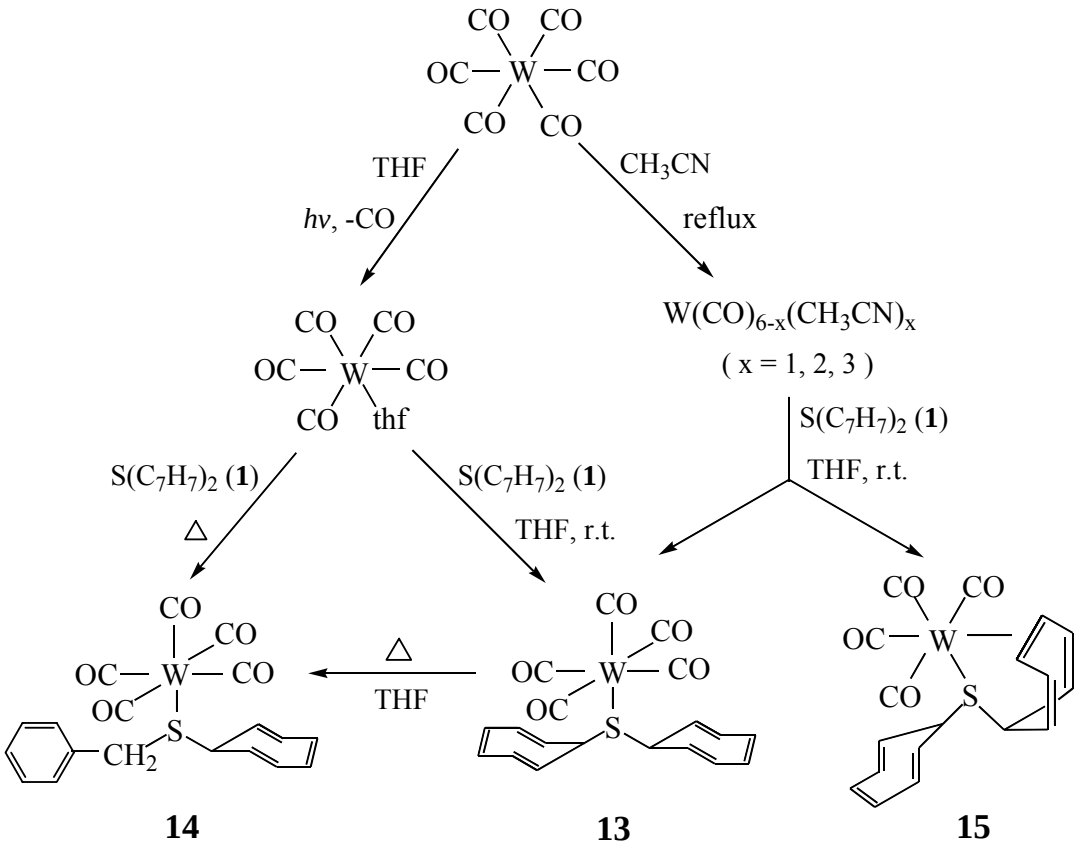


Fig.16. Synthesis of the complexes $W(CO)_5[S(C_7H_7)_2]$ (**13**), $W(CO)_5[PhCH_2S(C_7H_7)]$ **(14)** and $W(CO)_4[(\eta^2\text{-}C_7H_7)S(C_7H_7)]$ (**15**)

In **15** the olefinic sulfane $S(C_7H_7)_2$ plays the part of a 4-electron ligand, bearing one η^2-coordinated and one free cyclohepta-2,4,6-trienyl substituent at the sulfur atom. The structures of **13** and **15** were confirmed by X-ray crystallography (see below).

IR and NMR Spectroscopy

Table 16 contains the IR stretching frequencies of the carbonyl ligands (in pentane solution) and the ^1H and ^{13}C NMR data (in $CDCl_3$) for the carbonyltungsten compounds **13-15**.

Table 16. NMR Spectroscopic data of the tungsten complexes [a), b)]

	$W(CO)_5[S(C_7H_7)_2]$ **13**	$W(CO)_5[PhCH_2S(C_7H_7)]$ **14**	$W(CO)_4[(\eta^2\text{-}C_7H_7)S(C_7H_7)]$ **15**
^{1}H-NMR			
$\delta(H^1)$	4.02t (2H)	4.36t (1H)	3.92t (1H)
$\delta(H^2, H^7)$	5.54m (4H)	5.72dd (2H)	5.59m (2H)
$\delta(H^3, H^6)$	6.41m (4H)	6.50m (2H)	6.48m (2H)
$\delta(H^4, H^5)$	6.69m (4H)	6.74dd (2H)	6.68m (2H)
$\delta(H^{1'})$			4.94t (1H)
$\delta(H^{2'}, H^{7'})$			5.59m (2H)
$\delta(H^{3'}, H^{6'})$			6.68m (2H)
$\delta(H^{4'}, H^{5'})$			5.38br (2H)
$\delta(CH_2)$		4.08s (2H)	
δ(Ph)		7.20-7.31m (5H)	
^{13}C-NMR			
$\delta(C^1)$	49.7	53.2	43.7
$\delta(C^2, C^7)$	121.8	121.9	125.0
$\delta(C^3, C^6)$	128.9	129.6	130.1
$\delta(C^4, C^5)$	131.9	132.1	131.4
$\delta(C^{1'})$			48.2
$\delta(C^{2'}, C^{7'})$			125.7
$\delta(C^{3'}, C^{6'})$			132.7
$\delta(C^{4'}, C^{5'})$			77.2, 76.2

$\delta(CH_2)$ δ(Ph) δ(CO) [c)]	 197.3 [129.0] (cis) 199.5 [155.8] (trans)	45.5 128.3(p), 128.8(m), 129.7(o), 134.4(i) 197.0 [129.3] (cis) 199.9 (trans)	 203.6 [166.1] 203.3 [168.1]
IR: ν(CO) (cm^{-1}) (pentane)	2073(w), 1946(s), 1937(s), 1931(s)	2073(w), 1941(s), 1935(s), 1929(s)	2032(m), 1942(s), 1927(s), 1896(s)

a) NMR Data in $CDCl_3$ at 25 °C.

b) NMR Multiplicities: s singlet, dd doublet of doublets, t triplet, m multiplet.

c) Coupling constant, [$^1J(^{183}W, ^{13}C)$] [Hz].

The complexes **13** and **14** possess very similar IR band patterns. The number of ν(CO) bands observed for the complex **15** confirms the number of 4 CO ligands in a *cis*-$W(CO)_4$ arrangement.

The ^1H and ^{13}C NMR spectra of complex **13** are simple because the sulfane ligand, $S(C_7H_7)_2$, carries two uncoordinated cyclohepta-2,4,6-trienyl rings which give rise to four signals. Multiplets are observed for the protons H^2/H^7, H^3/H^6 and H^4/H^5 of the cyclohepta-2,4,6-trienyl substituents; the shift difference ($\Delta\delta$) of H^1 is about 0.4 ppm down-field compared to the free sulfane **1**.

In the ^1H NMR spectrum of complex **14** the benzyl group has similar chemical shifts as that in the chromium analogue **7**, $Cr(CO)_5[S(C_7H_7)CH_2Ph]$ ($\delta(CH_2)$ 3.88, δ(Ph) 7.27). The benzyl CH_2 group singlet of the coordinated $[S(C_7H_7)CH_2Ph]$ sulfane ligand is found at $\delta(CH_2)$ 4.08, compared to the free sulfane $S(CH_2Ph)_2$ ($\delta(CH_2)$ 3.59) [102].

For the chelate complex **15**, a total of ten ^{13}C NMR signals are observed, (*i.e.* 4 originating from the free seven-membered ring, 4 from the η^2-coordinated cyclohepta-2,4,6-trienyl ring and 2 from carbonyl groups). The signals of the coordinated double bond ($H^{4',5'}$ and $C^{4',5'}$) are shifted upfield ($\delta(H^{4',5'})$ 5.41, $\delta(C^{4',5'})$ 75.6) compared with the corresponding signals of the uncoordinated sulfane **1** ($\delta(H^{4,5})$ 6.58, $\delta(C^{4,5})$ 131.2).

Molecular Structures of $W(CO)_5[S(C_7H_7)_2]$ (13) and $W(CO)_4[(\eta^2\text{-}C_7H_7)S(C_7H_7)]$ (15)

The relevant distances and angles of the inner sphere around the central metal W are compiled for complex **13** in Table 17, the numbering system is given in Fig. 17. For complex **15** the distances and angles are given in Table 19 and the numbering system in Fig. 18.

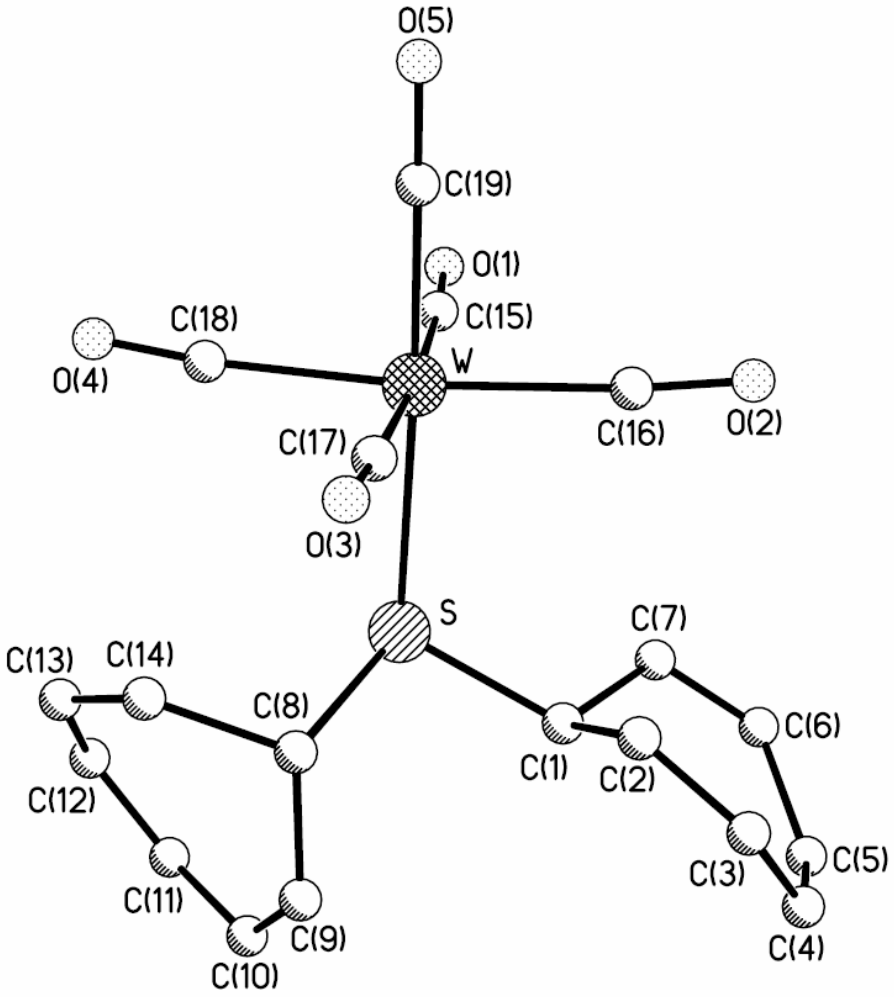


Fig.17. Structure of $W(CO)_5[S(C_7H_7)_2]$ (**13**)

Both structures **13** and **15** are dominated by the bulky $S(C_7H_7)_2$ ligand. The cycloheptatrienyl substituents generally assume the boat conformation.

In the crystal lattice of complex **13** the two substituents C_7H_7 have no connection with the tungsten atom to which the $S(C_7H_7)_2$ ligand is attached. One ring substituent (containing C(1)) is connected to the sulfur atom in an equatorial position, and the

other ring substituent (containing C(8)) is in an axial position. The angle of C(1)-S-C(8) (98.31(18)°) is slightly smaller than the corresponding angle in sulfane **1** (100.71(12)°). Compared with the bond length of S-C(1) (184.43(18) pm) in sulfane **1**, the bond distance of S-C(1) (182.6(4) pm) is shorter and the bond length of S-C(8) (187.3(4) pm) is longer in complex **13**. The carbonyl ligands are nearly linear (W-C-O angles 174.4-178.6°, av. 176.1(6)°). The CO ligand *trans* to sulfur is slightly closer to the metal (197.3(4) pm) than the other four carbonyl groups (W-C(15) 203.3(5) pm, W-C(16) 204.7(4) pm, W-C(17) 203.8(4) pm, W-C(18) 204.0(4) pm), and is slightly less bent (angle S-W-C(19) 177.55(11)°). The other four carbonyl groups are nearly coplanar, the dihedral angle between the plane C(15)-W-C(16) and the plane C(17)-W-C(18) is 4.3°.

Table 17. Relevant distances and angles of complex 13

Distances (pm)		Angles (°)	
W-C(19)	197.3(4)	C(19)-W-C(15)	89.80(17)
W-C(15)	203.3(5)	C(19)-W-C(17)	87.65(16)
W-C(17)	203.8(4)	C(15)-W-C(17)	175.88(15)
W-C(18)	204.0(4)	C(19)-W-C(18)	88.80(16)
W-C(16)	204.7(4)	C(15)-W-C(18)	85.02(17)
		C(17)-W-C(18)	91.69(16)
W-S	257.32(10)	C(19)-W-C(16)	87.92(16)
		C(15)-W-C(16)	88.61(18)
S-C(1)	182.6(4)	C(17)-W-C(16)	94.53(18)
S-C(8)	187.3(4)	C(18)-W-C(16)	172.84(16)
		C(19)-W-S	177.55(11)
O(1)-C(15)	113.6(6)	C(15)-W-S	91.44(12)
O(2)-C(16)	113.6(5)	C(17)-W-S	91.00(11)
O(3)-C(17)	114.1(5)	C(18)-W-S	89.20(11)
O(4)-C(18)	113.8(5)	C(16)-W-S	94.23(11)
O(5)-C(19)	116.3(5)	C(1)-S-C(8)	98.31(18)
		C(1)-S-W	112.71(12)
C(1)-C(2)	149.5(6)	C(8)-S-W	108.35(13)
C(1)-C(7)	150.0(5)	C(2)-C(1)-C(7)	108.7(3)
C(2)-C(3)	133.5(6)	C(2)-C(1)-S	115.0(3)
C(3)-C(4)	142.5(8)	C(7)-C(1)-S	111.1(3)

C(4)-C(5)	133.3(8)	C(3)-C(2)-C(1)	119.8(4)
C(5)-C(6)	145.6(8)	C(2)-C(3)-C(4)	125.1(5)
C(6)-C(7)	133.3(6)	C(5)-C(4)-C(3)	125.9(5)
C(8)-C(9)	149.9(6)	C(4)-C(5)-C(6)	126.4(4)
C(8)-C(14)	150.2(6)	C(7)-C(6)-C(5)	124.4(5)
C(9)-C(10)	131.5(7)	C(6)-C(7)-C(1)	119.7(4)
C(10)-C(11)	140.9(8)	C(9)-C(8)-C(14)	111.0(4)
C(11)-C(12)	131.6(8)	C(9)-C(8)-S	111.3(3)
C(12)-C(13)	142.4(9)	C(14)-C(8)-S	109.0(3)
C(13)-C(14)	135.2(8)	C(10)-C(9)-C(8)	126.0(4)
		C(9)-C(10)-C(11)	127.3(4)
		C(12)-C(11)-C(10)	127.1(6)
		C(11)-C(12)-C(13)	126.7(6)
		C(14)-C(13)-C(12)	127.3(5)
		C(13)-C(14)-C(8)	124.2(5)
		O(1)-C(15)-W	175.1(4)
		O(2)-C(16)-W	175.1(4)
		O(3)-C(17)-W	177.4(3)
		O(4)-C(18)-W	174.4(4)
		O(5)-C(19)-W	178.6(4)

The diffraction data and the refinement parameters for complex **13**, calculated from the X-ray structure analysis, are shown in Table 18.

Table 18. Crystal data and structure refinement for complex 13

Empirical formula	$C_{19}\ H_{14}\ O_5\ S\ W$
Formula weight	538.21
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions	a = 9.2049(16) Å α = 69.868(13)°
	b = 9.834(2) Å β = 70.009(10)°
	c = 12.0027(15) Å γ = 89.151(15)°
Volume	952.1(3) $Å^3$
Z	2
Density (calculated)	1.877 Mg/m^3
Absorption coefficient	6.201 mm^{-1}
F(000)	516
Crystal size	0.22 x 0.17 x 0.12 mm^3
θ range for data collection	1.94 to 25.00°
Index ranges	-10<h<1, -10<k<10, -14<l<13
Reflections collected	3609
Independent reflections	3043 [R(int) = 0.0311]
Completeness to θ = 25.00°	91.0 %
Absorption correction	Empirical
Max. and min. transmission	0.6969 and 0.4165
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3043 / 0 / 236
Goodness-of-fit on F^2	1.079
Final R indices [I > 2σ (I)]	R1 = 0.0184, wR2 = 0.0468
R indices (all data)	R1 = 0.0201, wR2 = 0.0478
Extinction coefficient	0.0097(4)
Largest diff. peak and hole	0.781 and -0.803 $e{\cdot}Å^{-3}$

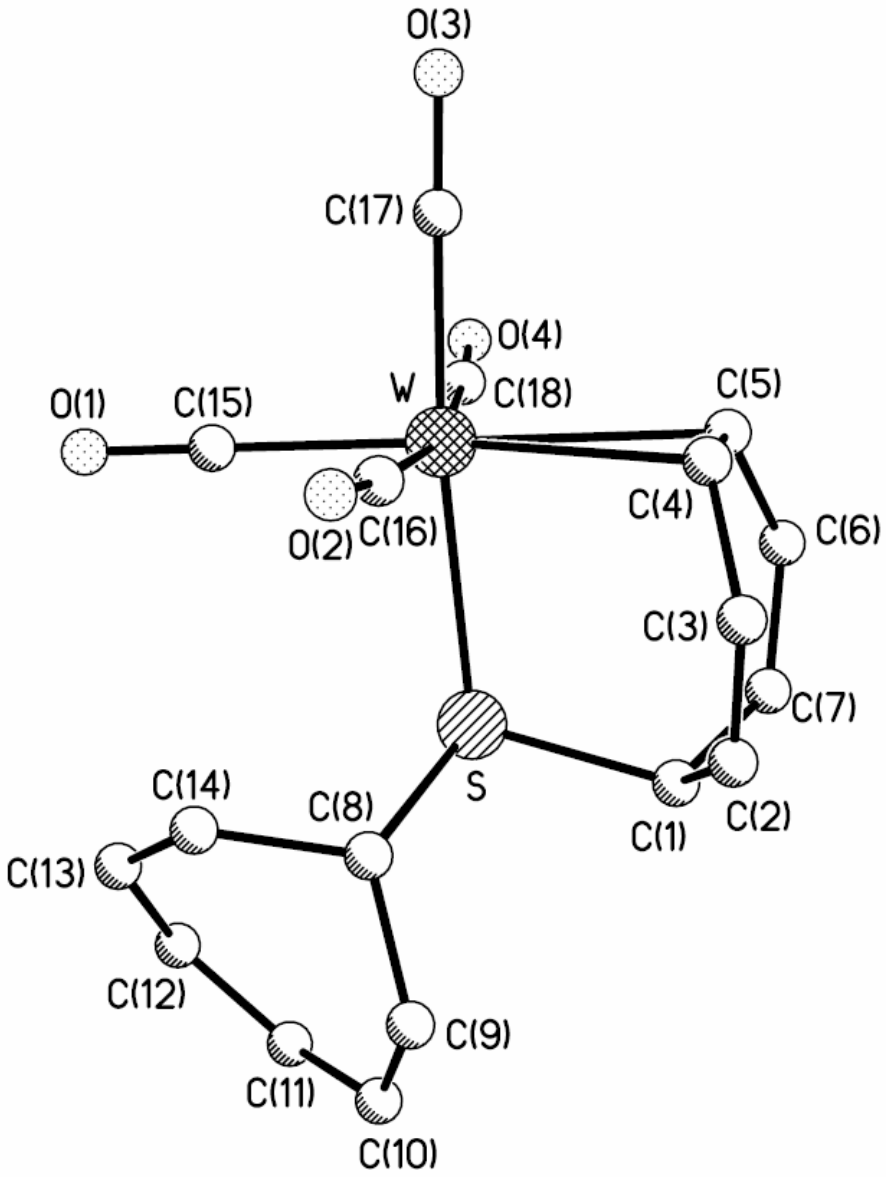


Fig.18. Structure of $W(CO)_4[(\eta^2\text{-}C_7H_7)S(C_7H_7)]$ (**15**)

In the complex **15** the sulfane ligand acts as a bidentate chelating ligand which occupies two of the six positions around the tungsten atom. The remaining four positions are taken by the carbonyl groups. The bond length of C(4)-C(5) (138.6(8) pm) is longer than the corresponding bond length in sulfane **1** (133.0(3) pm), and it appears to be widened as a result of π-complexation. The W-C(4) and W-C(5) bonds (η^2-coordinated C=C bond) are almost identical (246.0(5) pm and 247.0(5) pm), and they are longer than the W-CO bonds W-C(15), W-C(16), W-C(17) and W-C(18). The angle W-S-C(1) (107.86(16)°) involving the axially connected ring substituent is smaller than the angle W-S-C(8) (109.05(16)°). The angle of C(1)-S-C(8) is 99.1(2)°, which is slightly smaller than the corresponding angle in sulfane **1** (100.71(12)°). The

bond lengths of S-C(1) and S-C(8) are 185.2(5) pm and 186.0(5) pm, respectively, which are slightly longer than the corresponding bond length in sulfane **1** (184.43(18) pm). The CO ligand *trans* to sulfur comes slightly closer to the metal (195.7(5) pm) than the other three carbonyl groups (W-C(15) 199.1(6) pm, W-C(16) 202.8(5) pm, W-C(18) 202.1(5) pm), and is slightly less bent (angle S-W-C(17) 174.43(16)°). The coordinated double bond, C(4)-C(5) (138.6(8) pm), is essentially coplanar with the 3 carbonyl carbon atoms C(15)C(16)C(18); the dihedral angle between the vector C(4)-C(5) and this plane is 2.4°. The central metal W is part of the plane C(4)C(5)WC(15)O(1), whereas the two *cis*-carbonyl groups C(16)O(2) and C(18)O(4) are bent out by an angle C(16)-W-C(18) of 169.5(2)°. The bond distance W-S (252.85(11) pm) is shorter than the corresponding bond distance W-S in $W(CO)_5[S(C_7H_7)_2]$ (**13**) (257.32(10) pm), but longer than that in $CpWRe(\mu\text{-}SO_2Ph)(CCPh)(CO)_5$ (250.6(2) pm) [109].

Table 19. Relevant distances and angles of complex 15

Distances (pm)		Angles (°)	
W-C(17)	195.7(5)	C(17)-W-C(15)	92.3(2)
W-C(15)	199.1(6)	C(17)-W-C(18)	84.82(19)
W-C(18)	202.1(5)	C(15)-W-C(18)	87.6(2)
W-C(16)	202.8(5)	C(17)-W-C(16)	88.7(2)
W-C(4)	246.0(5)	C(15)-W-C(16)	84.5(2)
W-C(5)	247.0(5)	C(18)-W-C(16)	169.5(2)
		C(17)-W-C(4)	89.66(19)
W-S	252.85(11)	C(15)-W-C(4)	161.1(2)
		C(18)-W-C(4)	111.4(2)
S-C(1)	185.2(5)	C(16)-W-C(4)	76.8(2)
S-C(8)	186.0(5)	C(17)-W-C(5)	89.9(2)
		C(15)-W-C(5)	166.0(2)
O(1)-C(15)	113.0(7)	C(18)-W-C(5)	78.9(2)
O(2)-C(16)	113.4(6)	C(16)-W-C(5)	109.4(2)
O(3)-C(17)	116.3(6)	C(4)-W-C(5)	32.66(18)
O(4)-C(18)	114.8(7)	C(17)-W-S	174.43(16)
		C(15)-W-S	92.80(17)
C(1)-C(2)	148.8(7)	C(18)-W-S	93.19(14)
C(1)-C(7)	151.2(7)	C(16)-W-S	94.01(15)

C(2)-C(3)	130.6(7)	C(4)-W-S	86.22(13)
C(3)-C(4)	146.7(7)	C(5)-W-S	84.63(13)
C(4)-C(5)	138.6(8)	C(1)-S-C(8)	99.1(2)
C(5)-C(6)	145.8(8)	C(1)-S-W	107.86(16)
C(6)-C(7)	131.7(8)	C(8)-S-W	109.05(16)
C(8)-C(9)	147.5(7)	C(2)-C(1)-C(7)	112.1(4)
C(8)-C(14)	148.2(7)	C(2)-C(1)-S	112.6(3)
C(9)-C(10)	133.8(10)	C(7)-C(1)-S	106.7(3)
C(10)-C(11)	142.3(11)	C(3)-C(2)-C(1)	124.8(5)
C(11)-C(12)	134.1(11)	C(2)-C(3)-C(4)	127.1(5)
C(12)-C(13)	143.8(10)	C(5)-C(4)-C(3)	125.0(5)
C(13)-C(14)	131.7(8)	C(5)-C(4)-W	74.1(3)
		C(3)-C(4)-W	114.1(3)
		C(4)-C(5)-C(6)	125.1(5)
		C(4)-C(5)-W	73.3(3)
		C(6)-C(5)-W	114.7(3)
		C(7)-C(6)-C(5)	127.9(5)
		C(6)-C(7)-C(1)	123.3(5)
		C(9)-C(8)-C(14)	111.0(4)
		C(9)-C(8)-S	112.3(4)
		C(14)-C(8)-S	108.8(3)
		C(10)-C(9)-C(8)	125.6(6)
		C(9)-C(10)-C(11)	125.9(6)
		C(12)-C(11)-C(10)	126.5(7)
		C(11)-C(12)-C(13)	126.3(7)
		C(14)-C(13)-C(12)	126.9(6)
		C(13)-C(14)-C(8)	125.3(5)
		O(1)-C(15)-W	179.5(7)
		O(2)-C(16)-W	174.5(5)
		O(3)-C(17)-W	178.1(5)
		O(4)-C(18)-W	174.0(5)

The diffraction data and the refinement parameters for complex **15**, calculated from the X-ray structure analysis, are shown in Table 20.

Table 20. Crystal data and structure refinement for complex 15

Empirical formula	$C_{18}\,H_{14}\,O_4\,S\,W$
Formula weight	510.20
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 15.9644(19) Å α = 90°
	b = 9.3841(6) Å β = 102.316(7)°
	c = 11.9344(10) Å γ = 90°
Volume	1746.8(3) $Å^3$
Z	4
Density (calculated)	1.940 Mg/m^3
Absorption coefficient	6.750 mm^{-1}
F(000)	976
Crystal size	0.25 x 0.18 x 0.10 mm^3
θ range for data collection	2.53 to 25.00°
Index ranges	-18<h<18, -11<k<1, -14<l<1
Reflections collected	3987
Independent reflections	3056 [R(int) = 0.0400]
Completeness to θ = 25.00°	99.5 %
Absorption correction	Empirical
Max. and min. transmission	0.3379 and 0.2227
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3056 / 0 / 218
Goodness-of-fit on F^2	1.052
Final R indices [I > 2σ (I)]	R1 = 0.0251, wR2 = 0.0659
R indices (all data)	R1 = 0.0293, wR2 = 0.0685
Extinction coefficient	0.0029(2)
Largest diff. peak and hole	1.617 and -1.148 $e{\cdot}Å^{-3}$

3.4 Carbonylmanganese Complexes

Synthesis

When dimanganese decacarbonyl, $Mn_2(CO)_{10}$, reacted with di(1-cyclohepta-2,4,6-trienyl) thioether (**1**) in THF solution under irradiation, a dimeric complex, $Mn_2(CO)_8[S(C_7H_7)]_2$ (**17**), was obtained. In this new complex the sulfur ligand has changed, one ring substituent had been lost from the sulfane ligand and ditropyl had been formed.

Dimanganese decacarbonyl can be split with chlorine or bromine to give the pentacarbonylmanganese halides [110]. We expected that the halide in $Mn(CO)_5X$ might be replaced by the sulfane **1** to give the complex **16**. However, the dimer **17** was again obtained. In addition, two carbonyl groups of the dimer **17** could be replaced by two-electron ligands such as *tert*-butyl isocyanide and trimethyl phosphite (^{t}BuNC and $P(OMe)_3$) to give the derivatives $Mn_2(CO)_6[^t BuNC]_2[S(C_7H_7)]_2$ (**18**) and $Mn_2(CO)_6[P(OMe)_3]_2[S(C_7H_7)]_2$ (**19**) (Fig. 19).

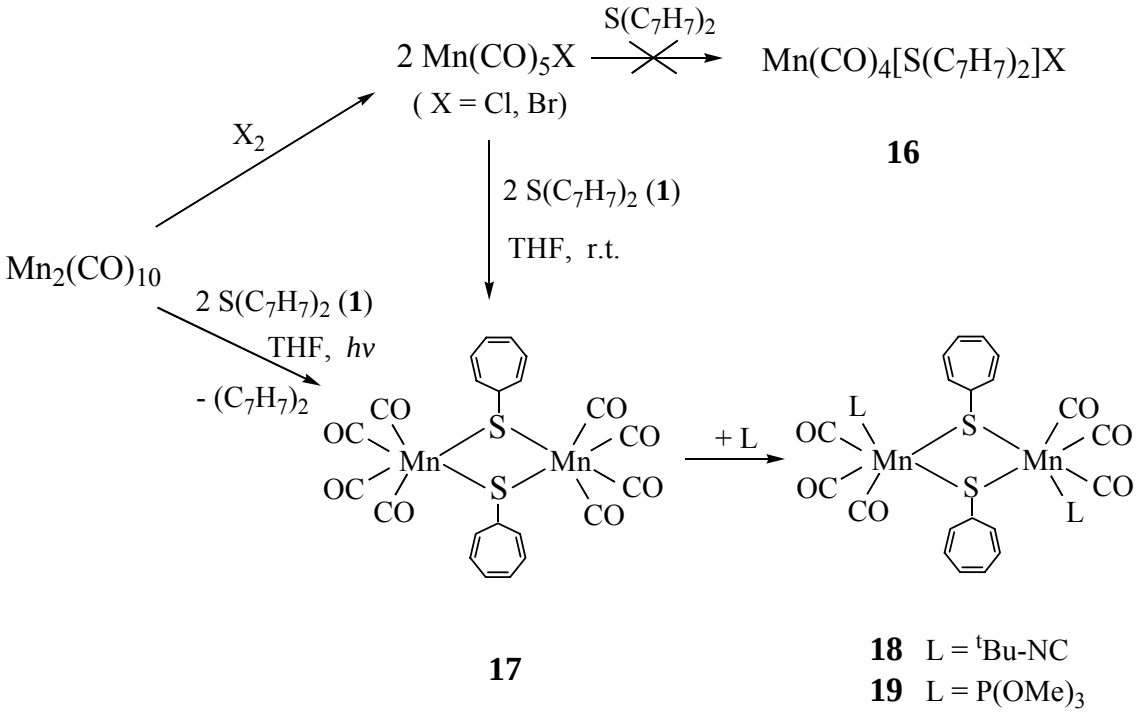


Fig.19. Synthesis of the complexes $Mn_2(CO)_8[S(C_7H_7)]_2$ (**17**), $Mn_2(CO)_6[^t BuNC]_2[S(C_7H_7)]_2$ (**18**) and $Mn_2(CO)_6[P(OMe)_3]_2[S(C_7H_7)]_2$ (**19**)

Starting from $CpMn(CO)_3$, the photo-induced elimination of a single CO ligand leads to the thf-stabilized fragment $[CpMn(CO)_2]$. In the following dark reaction with di(1-cyclohepta-2,4,6-trienyl) thioether (**1**), attempts to displace the thf ligand and thus to attach **1** to the metal were not successful. Instead, the products **21** and **22** were isolated (Fig. 20), which had been reported before [111].

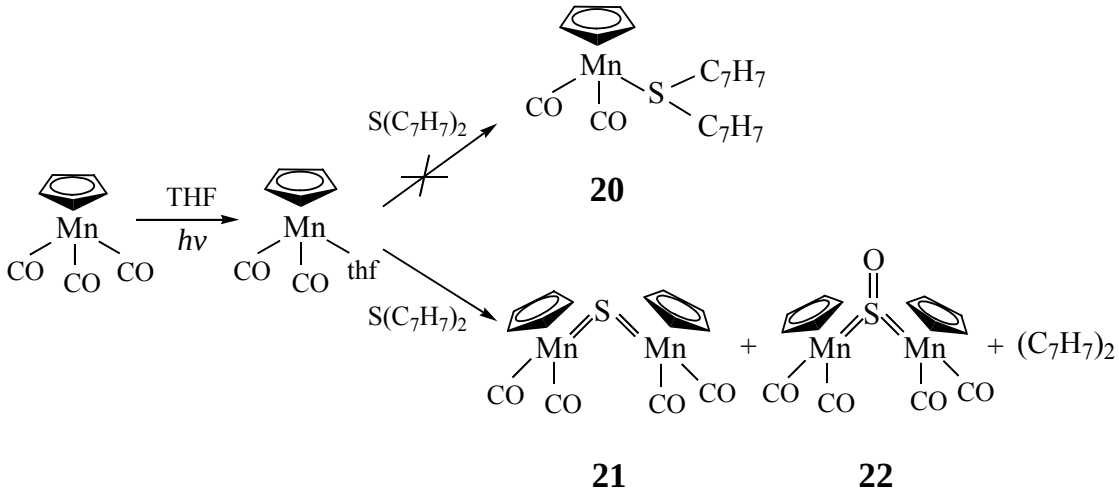


Fig.20. Reaction of $CpMn(CO)_3$ with $S(C_7H_7)_2$ to give complexes **21** and **22**

IR and NMR Spectroscopy

Table 21 contains the IR stretching frequencies of the carbonyl ligands (in pentane solution) and the ^1H and ^{13}C NMR data (in $CDCl_3$) for the compounds **17**-**19**.

The ν(CO) stretching absorptions consistently indicate the presence of only terminal carbonyl ligands, also in the dinuclear compound **17**. The electron-donating *tert*-butyl isocyanide and trimethyl phosphite ligands (^{t}BuNC and $P(OMe)_3$) in **18**, **19** shift the ν(CO) pattern to lower wave-numbers.

Table 21. NMR Spectroscopic data of the manganese complexes [a), b)]

	$Mn_2(CO)_8[S(C_7H_7)]_2$ **17**	$Mn_2(CO)_6[^tBuNC]_2[S(C_7H_7)]_2$ **18** [c)]	$Mn_2(CO)_6[P(OMe)_3]_2[S(C_7H_7)]_2$ **19**
^1H-NMR			
$\delta(H^1)$	3.92t (2H)	3.03t (2H)	4.35t (2H)
$\delta(H^2, H^7)$	5.59t (4H)	5.24m (4H)	5.94t (4H)
$\delta(H^3, H^6)$	6.24m (4H)	6.16m (4H)	6.17m (4H)
$\delta(H^4, H^5)$	6.65s (4H)	6.68m (4H)	6.41s (4H)

δ(^{t}Bu)		1.58s (18H)	
δ(Me)			3.66, 3,61m (18H)
^{13}C-NMR			
δ(C^1)	46.2	45.6	46.5
δ(C^2, C^7)	125.0	124.1	127.8
δ(C^3, C^6)	128.3	128.2	128.2
δ(C^4, C^5)	131.7	131.0	130.8
δ(CMe$_3$)		58.2	
δ(Me)		30.6	52.0 [3.18] [d]
δ(CO)	212.3, 214.5	216.4, 219.5	
^{31}P-NMR			172.6
IR: ν(CO) (cm^{-1}) (pentane)	2069(w), 2012(s), 1999(s), 1965(s)	2013(s), 1952(s), 1930(s) 2160(w) ν(N≡C)	2046(m), 2015(s), 1984(m)

a) NMR Data in $CDCl_3$ at 25 °C.

b) NMR Multiplicities: s singlet, d doublet, dt doublet of triplets, t triplet, m multiplet.

c) cf. *tert*-butyl isocyanide: ^{1}H-NMR ($CDCl_3$): δ(Me) 1.45; ^{13}C-NMR ($CDCl_3$): δ(Me) 30.8, δ(CN) 153.4; IR (Film): ν(C≡N) 2136 cm^{-1}.

d) Coupling constant, [^2J(^{31}P, ^{13}C)] [Hz].

The ^{1}H and ^{13}C NMR spectra of the compounds **17**, **18** and **19** are simple and clear because in the dimeric thiolato-bridged complexes the sulfur atom carries only one uncoordinated cyclohepta-2,4,6-trienyl ring which gives rise to four signals. For complex **18** the signal of H^1 is shifted upfield by about 0.6 ppm compared with the free sulfane **1**. But the signals of H^1 in **17** and **19** are shifted downfield relative to the sulfane **1**.

Molecular Structures of $Mn_2(CO)_8[\mu\text{-}S(C_7H_7)]_2$ (17) and $Mn_2(CO)_6[^t\text{BuNC}]_2[\mu\text{-}S(C_7H_7)]_2$ (18)

The molecular structures of the complexes $Mn_2(CO)_8[\mu\text{-}S(C_7H_7)]_2$ (**17**) and $Mn_2(CO)_6[^t\text{BuNC}]_2[\mu\text{-}S(C_7H_7)]_2$ (**18**) are illustrated in Figs. 21 and 22. Relevant distances and angles are given in Tables 23 and 25.

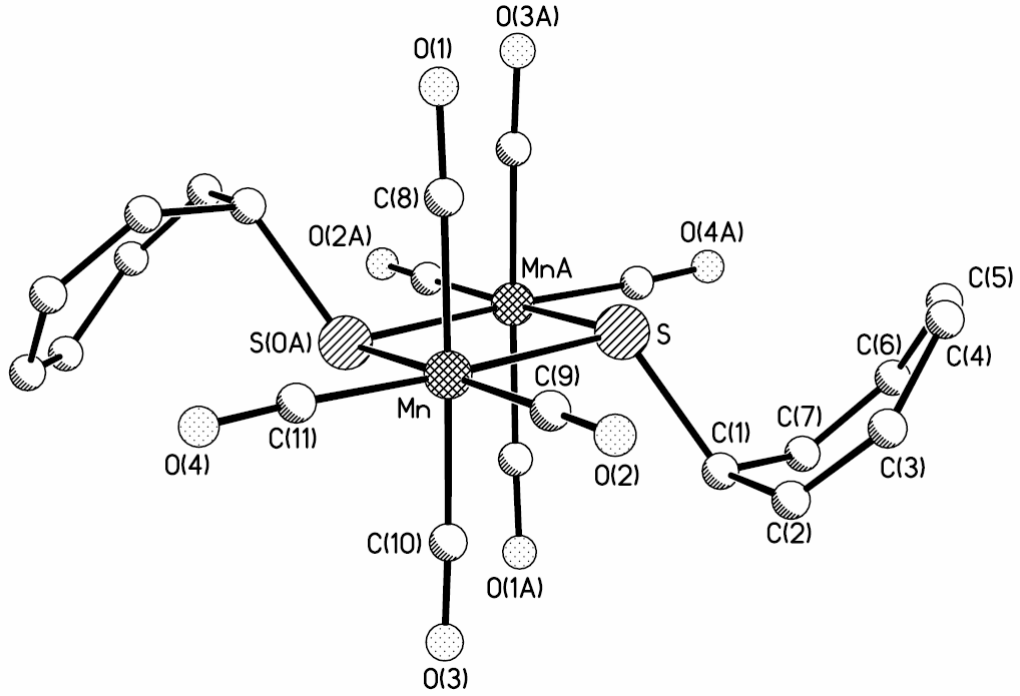


Fig.21. Structure of $Mn_2(CO)_8[\mu\text{-}S(C_7H_7)]_2$ (**17**)

In the dinuclear complex **17** the two metal centers are connected via 2 bridges, formed by two sulfur atoms. These four atoms form the central Mn_2S_2 plane. The distance of the two manganese atoms (361.0 pm) is shorter than the Mn-Mn distance in the dimer $[Mn(CO)_4(SPh)]_2$ (376.3(1) pm) [112], and is much longer than the Mn-Mn single bond in the parent $Mn_2(CO)_{10}$ (290.38(6) pm) [113]. The bond length of S-C(1) is 187.2(2) pm, which is a little longer than the corresponding bond length in sulfane **1** (184.43(18) pm). The Mn-S distances are observed at 238.94(7) pm and 238.66(8) pm, they are comparable with the average Mn-S bond distance in the dimers $[Mn(CO)_4(SPh)]_2$ (239.3 pm) [112] and $[Mn(CO)_4(SC_6H_4CH_3)]_2$ (239.7(1) pm) [114], but slightly longer than those in various sulfane and thiolato complexes (Table 22). The S-C bond distance in **17** is 187.2(2) pm, slightly longer than the S-C bond distances in dimer $[Mn(CO)_4(SPh)]_2$ (178.4(7) and 179.3(9) pm) [112]. The carbonyl ligands in complex **17** are nearly linear (Mn-C-O angles 176.1-178.6°, av. 177.4(2)°). The CO ligands *trans* to sulfur are slightly closer to the metal (Mn-C(9) 183.4(3) pm, Mn-C(11) 182.0(2) pm) than the two other carbonyl groups (Mn-C(8) 186.2(2) pm, Mn-C(10) 185.0(2) pm). Compared with the parent sulfane $S(C_7H_7)_2$ (**1**), there is only one cycloheptatrienyl substituent left and this assumes the boat conformation. This dimer possesses a center of symmetry; the angles in the central Mn_2S_2 plane are 98.21(2)° at the S atoms and 81.79(2)° at the Mn atoms.

Table 22. Comparison of bond distances and angles in various manganese complexes

Complex	d(Mn-S) (pm) (bridges)	d(Mn···Mn) (pm)	S-Mn-S (°)	Mn-S-Mn (°)	Lit.
$[Mn(CO)_4(\mu\text{-}SC_7H_7)]_2$ (**17**)	238.94(7) 238.66(8)	361.0	81.79(2)	98.21(2)	a)
$[Mn(CO)_3(CN^tBu)(\mu\text{-}SC_7H_7)]_2$ (**18**)	241.44(13) 240.49(11)	363.4	82.12(4)	97.88(4)	a)
$[Mn(CO)_4(\mu\text{-}SPh)]_2$	240.1(2) 238.9(2)				[112]
	av. 240.0(1)	362.06(7)	81.77(3) 81.71(3)	98.59(3) 97.29(3)	[114]
$[Mn(CO)_4(\mu\text{-}SC_6H_4Me(p))]_2$	*av.* 239.7(1)		82.4(1) 82.3(1)	98.1(1) 97.0(1)	[115]
$[Mn(CO)_4(\mu\text{-}SR)_2]_2Ni$ (R = 2-thienyl, C_4H_3S)	239.1(1) 238.2(1)	[336.4] (Mn-Ni)	77.28(3)		[116]
$\{[Mn(CO)_3]_2(\mu\text{-}SPh)_3\}^-(NBu_4^+)$	239.1(1)-240.3(1)	318.5(2)	*av.* 80.7(1)	83.1(1) 83.1(1) 83.3(1)	[117]
$MnFe(CO)_6(\mu\text{-}SPh)_3$	239.3(2) 237.5(2) 237.0(2)	[312.9(1)] (Mn-Fe)	*av.* 79.7(7)		[118]
$[Mn(CO)_2(PMe_3)]_2(\mu\text{-}SMe)_2(\mu\text{-}CO)$	*av.* 233.0(1)	258.1(1)	74.81(3) 74.72(3)	67.39 67.19	[119]
$\{[CpMn(CO)_2]_2(\mu\text{-}SEt)\}^+(ClO_4^-)$	227.0(2) 224.2(2)	293.0(1)		81.0(1)	[120]

$\{[CpMn(CO)_2]_2(\mu\text{-}S^tBu)\}^+ (PF_6^-)$	226.7(1) 226.1(1)	296.2(1)		81.7(1)	[121]
$\{[CpMn(CO)_2]_2(\mu\text{-}SPh)\}^+ (PF_6^-)$	218.9(2)	b)		143.6(1)	[122]
$\{[CpMn(CO)_2]_2(\mu\text{-}SC_6H_4NO_2(p))\}^+ (PF_6^-)$	217.8(3)	(403.2 / 404.6) [b]		135.0(1) / 136.6(1)	[121]
$[(\eta^6\text{-}C_6H_3Me_3)Mn(CO)_2]_2(\mu\text{-}SPh)\}^+ (PF_6^-)$	235.7(2) 234.7(2)	(414.9) [b]		123.8(1)	[123]
$[CpMn_2(CO)_5](\mu\text{-}S^tBu)(\mu\text{-}CO)$	226.2(2) 225.0(2)	278.2(2)		76.1(1)	[124]
$[Mn(CO)_4]_2(\mu\text{-}S(CH_2)_4)$	223.3(3) 222.4(3)	281.5(3)		78.3(1)	[125]
$[Mn(CO)_4]_2(\mu\text{-}S(CH_2)_2CMe_2)$	221.1(1) 220.7(1)	282.43(9)		79.48(4)	[126]
$[CpMn(CO)_2]_2(\mu\text{-}S(CH_2)_3)$	225.7(1)	b)		126.4	[127]
$[CpMn(CO)_2]_2(\mu\text{-}SMe_2)$				125.1	[128]
$\{[Mn(SPh)_2(\mu\text{-}SPh)]_2\}^{2-} (PPh_4^+)_2$	249.6(1) 248.9(1) [*av.* 239.6(1)-term.]	338.1(1)	94.6(1)	85.4(1)	[129]
$[Mn(SAr)_2]_2$ (Ar = 2,4,6-$C_6H_2{}^tBu_3$)	244.6(3) 244.0(3) [231.7(3)-term.]	355.4	86.7(1)	93.3(1)	[130]
$Mn_2(CO)_{10}$		290.38(6)			[113]
$CpMn(CO)_2SPh$ [c]	217.7(2)				[121]
$CpMn(CO)_2SC_6F_5$ [c]	220.5(3)				[121]
$Cp^*Mn(CO)_2S^tBu$ [c]	218.7(5)				[131]
$(\eta^6\text{-}C_6H_6)Mn(CO)_2SPh$	235.0(3)				[123]

a) This work. b) Open form. c) Radical.

Table 23. Relevant distances and angles of complex 17

Distances (pm)		Angles (°)	
Mn-C(11)	182.0(2)	C(11)-Mn-C(9)	90.16(10)
Mn-C(9)	183.4(3)	C(11)-Mn-C(10)	90.09(9)
Mn-C(10)	185.0(2)	C(9)-Mn-C(10)	92.63(10)
Mn-C(8)	186.2(2)	C(11)-Mn-C(8)	91.63(9)
Mn-S(OA)	238.66(8)	C(9)-Mn-C(8)	92.17(11)
Mn-S	238.94(7)	C(10)-Mn-C(8)	174.90(11)
Mn(A)-S	238.66(8)	C(11)-Mn-S(OA)	94.40(8)
		C(9)-Mn-S(OA)	174.46(7)
S-C(1)	187.2(2)	C(10)-Mn-S(OA)	84.23(8)
		C(8)-Mn-S(OA)	90.85(8)
O(1)-C(8)	113.8(3)	C(11)-Mn-S	175.77(8)
O(2)-C(9)	114.0(3)	C(9)-Mn-S	93.74(7)
O(3)-C(10)	114.1(3)	C(10)-Mn-S	91.36(7)
O(4)-C(11)	114.6(3)	C(8)-Mn-S	86.60(7)
		S(OA)-Mn-S	81.79(2)
C(1)-C(2)	148.2(4)	C(1)-S-Mn(A)	110.86(8)
C(1)-C(7)	149.5(3)	C(1)-S-Mn	109.36(7)
C(2)-C(3)	132.8(4)	Mn(A)-S-Mn	98.21(2)
C(3)-C(4)	143.6(4)		
C(4)-C(5)	134.3(4)	C(2)-C(1)-C(7)	111.93(19)
C(5)-C(6)	142.2(4)	C(2)-C(1)-S	109.28(15)
C(6)-C(7)	134.0(4)	C(7)-C(1)-S	110.71(15)
		C(3)-C(2)-C(1)	125.3(2)
Mn····Mn(A)	361.0	C(2)-C(3)-C(4)	128.0(3)
S····S(OA)	312.7	C(5)-C(4)-C(3)	126.0(3)
		C(4)-C(5)-C(6)	126.4(3)
		C(7)-C(6)-C(5)	127.7(2)
		C(6)-C(7)-C(1)	125.2(2)
		O(1)-C(8)-Mn	178.6(2)
		O(2)-C(9)-Mn	177.0(2)
		O(3)-C(10)-Mn	177.9(2)
		O(4)-C(11)-Mn	176.1(2)

The diffraction data and the refinement parameters for complex **17**, calculated from the X-ray structure analysis, are shown in Table 24.

Table 24. Crystal data and structure refinement for complex 17

Empirical formula	$C_{22}\ H_{14}\ Mn_2\ O_8\ S_2$
Formula weight	580.33
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 9.0389(18) Å α = 90°
	b = 11.873(2) Å β = 111.309(12)°
	c = 11.6227(19) Å γ = 90°
Volume	1162.1(4) $Å^3$
Z	2
Density (calculated)	1.659 Mg/m^3
Absorption coefficient	1.312 mm^{-1}
F(000)	584
Crystal size	0.18 x 0.16 x 0.11 mm^3
θ range for data collection	2.47 to 25.00°
Index ranges	-1<h<8, -14<k<1, -13<l<13
Reflections collected	2445
Independent reflections	1803 [R(int) = 0.0120]
Completeness to θ = 25.00°	88.1 %
Absorption correction	Empirical
Max. and min. transmission	0.4300 and 0.3343
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1803 / 0 / 154
Goodness-of-fit on F^2	1.034
Final R indices [I > 2σ (I)]	R1 = 0.0261, wR2 = 0.0684
R indices (all data)	R1 = 0.0312, wR2 = 0.0718
Largest diff. peak and hole	0.339 and -0.390 $e{\cdot}Å^{-3}$

The dinuclear complex **18** has the same centrosymmetric structure as complex **17**. Two carbonyl groups perpendicular to the plane MnSMn(A)S(OA) are replaced by ^{t}BuNC, and these two *tert*-butyl isocyanide groups protrude from the plane MnSMn(A)S(OA) into different directions, being arranged either above or below. The distance of the two manganese atoms (363.4 pm) is a little longer than the Mn-Mn distance in complex **17** (361.0 pm) and shorter than the Mn-Mn distance in the dimer $[Mn(CO)_4(SPh)]_2$ (376.3(1) pm) [112], and is much longer than the Mn-Mn single bond in $Mn_2(CO)_{10}$ (290.38(6) pm) [113]. The other carbonyl groups are nearly linear (Mn-C-O angles 176.1-177.3°, av. 176.8°). The CO ligands *trans* to sulfur are again slightly closer to the metal (Mn-C(9) 179.8(5) pm, Mn-C(10) 180.0(4) pm) than the other carbonyl group (Mn-C(8) 182.5(4) pm). The carbonyl groups *trans* to *tert*-butyl isocyanide are also closer to the metal (Mn-C(8) 182.5(4) pm) if compared with the corresponding Mn-CO distance in the unsubstituted complex **17** (185.0(2) pm, 186.2(2) pm). The bond distance of S-C(1) is 183.6(4) pm, which is shorter than the corresponding bond length in sulfane **1** (184.43(18) pm) and in complex **17** (187.2(2) pm).

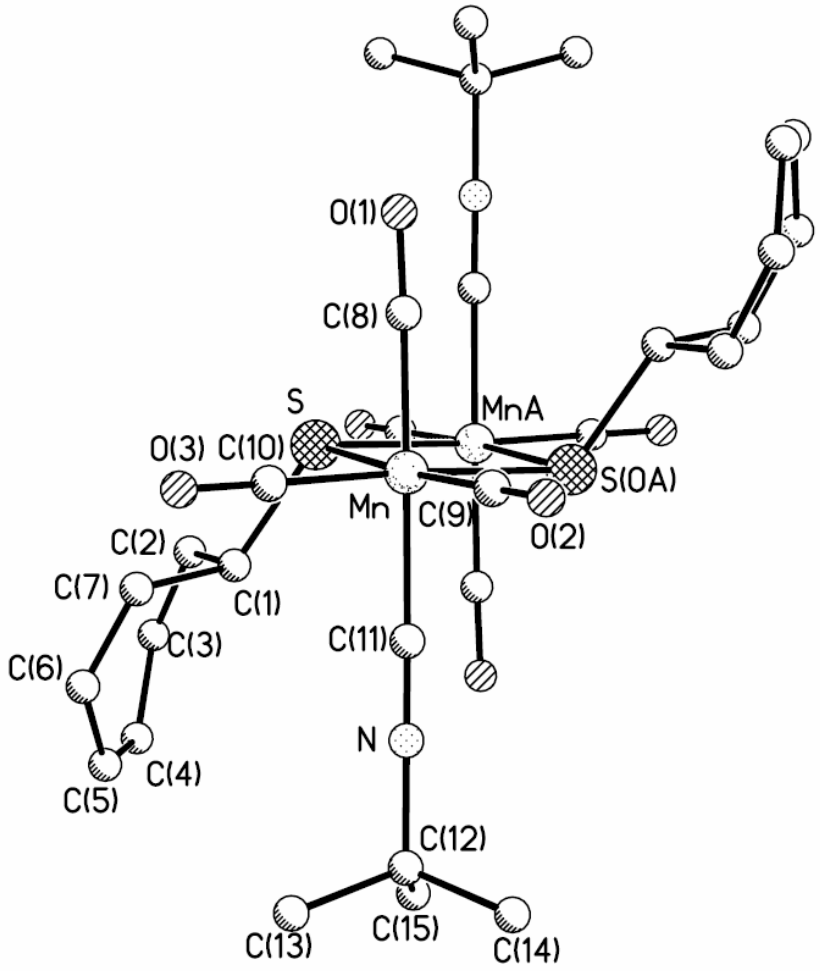


Fig.22. Structure of $Mn_2(CO)_6[^tBuNC]_2[\mu\text{-}S(C_7H_7)]_2$ (**18**)

Table 25. Relevant distances and angles of complex 18

Distances (pm)		Angles (°)	
Mn-C(9)	179.8(5)	C(9)-Mn-C(10)	89.63(17)
Mn-C(10)	180.0(4)	C(9)-Mn-C(8)	90.87(17)
Mn-C(8)	182.5(4)	C(10)-Mn-C(8)	89.86(17)
Mn-C(11)	195.8(4)	C(9)-Mn-C(11)	90.23(16)
Mn-S(OA)	240.49(11)	C(10)-Mn-C(11)	90.06(15)
Mn-S	241.44(13)	C(8)-Mn-C(11)	178.89(17)
Mn(A)-S	240.49(11)	C(9)-Mn-S(OA)	93.71(13)
		C(10)-Mn-S(OA)	175.17(12)
S-C(1)	183.6(4)	C(8)-Mn-S(OA)	93.57(12)
		C(11)-Mn-S(OA)	86.45(11)
N-C(11)	115.2(4)	C(9)-Mn-S	175.23(14)
N-C(12)	146.5(4)	C(10)-Mn-S	94.67(12)
		C(8)-Mn-S	87.09(13)
O(1)-C(8)	114.9(4)	C(11)-Mn-S	91.82(11)
O(2)-C(9)	116.8(5)	S(OA)-Mn-S	82.12(4)
O(3)-C(10)	115.7(4)	C(1)-S-Mn(A)	108.92(12)
		C(1)-S-Mn	110.23(12)
C(1)-C(2)	149.5(5)	Mn(A)-S-Mn	97.88(4)
C(1)-C(7)	149.7(5)	C(11)-N-C(12)	176.1(4)
C(2)-C(3)	134.4(5)	C(2)-C(1)-C(7)	106.3(3)
C(3)-C(4)	142.8(6)	C(2)-C(1)-S	112.1(3)
C(4)-C(5)	133.9(6)	C(7)-C(1)-S	113.1(2)
C(5)-C(6)	143.4(5)	C(3)-C(2)-C(1)	119.7(4)
C(6)-C(7)	133.1(5)	C(2)-C(3)-C(4)	124.5(4)
C(12)-C(14)	151.3(5)	C(5)-C(4)-C(3)	126.1(4)
C(12)-C(13)	151.5(6)	C(4)-C(5)-C(6)	125.0(4)
C(12)-C(15)	151.8(6)	C(7)-C(6)-C(5)	125.2(4)
		C(6)-C(7)-C(1)	120.0(3)
Mn····Mn(A)	363.4	O(1)-C(8)-Mn	176.9(4)
S····S(OA)	316.6	O(2)-C(9)-Mn	176.1(4)
		O(3)-C(10)-Mn	177.3(3)
		N-C(11)-Mn	176.0(3)

		N-C(12)-C(14)	106.5(3)
		N-C(12)-C(13)	107.0(3)
		N-C(12)-C(15)	108.1(3)
		C(14)-C(12)-C(13)	111.3(4)
		C(14)-C(12)-C(15)	111.5(3)
		C(13)-C(12)-C(15)	112.1(4)

The diffraction data and the refinement parameters for complex **18**, calculated from the X-ray structure analysis, are shown in Table 26.

Table 26. Crystal data and structure refinement for complex 18

Empirical formula	$C_{30}\ H_{32}\ Mn_2\ N_2\ O_6\ S_2$
Formula weight	690.43
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 9.852(2) Å α = 90°
	b = 11.535(2) Å β = 98.67(3)°
	c = 17.925(4) Å γ = 90°
Volume	2013.9(7) $Å^3$
Z	2
Density (calculated)	1.419 Mg/m^3
Absorption coefficient	1.037 mm^{-1}
F(000)	880
Crystal size	0.17 x 0.16 x 0.06 mm^3
θ range for data collection	2.09 to 26.03°
Index ranges	-12<h<12, -14<k<13, -21<l<22
Reflections collected	13705
Independent reflections	3901 [R(int) = 0.0827]
Completeness to θ = 26.03°	98.0 %
Absorption correction	Numerical
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3901 / 0 / 217
Goodness-of-fit on F^2	0.700
Final R indices [I > 2σ (I)]	R1 = 0.0409, wR2 = 0.0862
R indices (all data)	R1 = 0.0989, wR2 = 0.0988
Largest diff. peak and hole	0.513 and -0.313 e·$Å^{-3}$

3.5 Carbonyliron Complex

Synthesis

The photo-induced method used for the preparation of new chromium, molybdenum and tungsten complexes was also applied to $Fe_3(CO)_{12}$, which was irradiated in THF solution to generate the $Fe(CO)_4$(thf). In the subsequent dark reaction, the thf ligand was displaced by $S(C_7H_7)_2$ (**1**). The product is tentatively assumed to be the expected monosubstituted derivative $Fe(CO)_4[S(C_7H_7)_2]$ (**23**), in which the two seven-membered ring substituents are freely pending (Fig. 23).

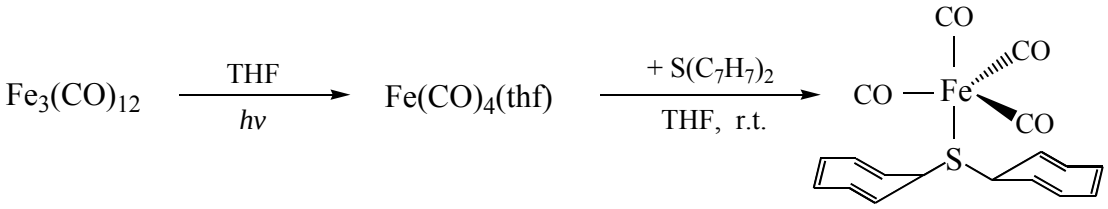


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Fig.23. Synthesis of the complex $Fe(CO)_4[S(C_7H_7)_2]$ (**23**)

IR and NMR Spectroscopy

Table 27 contains the IR stretching frequencies of the carbonyl ligands (in pentane solution) and the ^1H and ^{13}C NMR data (in $CDCl_3$) for the complex **23**.

Table 27. NMR Spectroscopic data of the iron complex 23 [a), b)]

$Fe(CO)_4[S(C_7H_7)_2]$ (**23**)			
^1H-NMR		^{13}C-NMR	
$\delta(H^1)$	4.17t (2H)	$\delta(C^1)$	49.9
$\delta(H^2, H^7)$	5.65m (4H)	$\delta(C^2, C^7)$	124.8
$\delta(H^3, H^6)$	6.28m (4H)	$\delta(C^3, C^6)$	128.3
$\delta(H^4, H^5)$	6.57t (4H)	$\delta(C^4, C^5)$	131.6
IR: ν(CO) (cm^{-1}) (pentane)	2063(s), 2045(s), 2025(m), 2008(w)		

a) NMR Data in $CDCl_3$ at 25 °C.

b) NMR Multiplicities: s singlet, d doublet, t triplet, m multiplet.

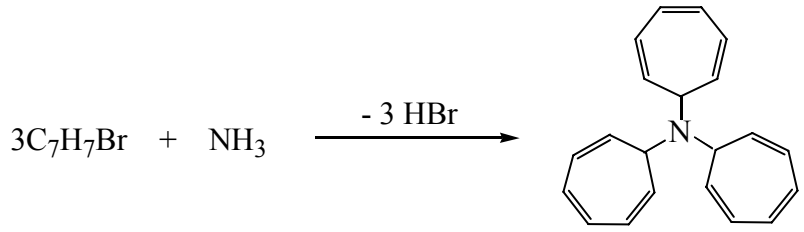
The IR pattern of the ν(CO) stretching absorptions indicates 4 carbonyl ligands. The ^{1}H and ^{13}C NMR spectra of complex **23** are easy to explain because the sulfane ligand, $S(C_7H_7)_2$, carries two uncoordinated cyclohepta-2,4,6-trienyl rings which give rise to four signals. The shift difference (Δδ) of H^{1} is about 0.5 ppm down-field compared with the uncoordinated sulfane **1**.

Chapter 4

Investigations with Tri(1-cyclohepta-2,4,6-trienyl) amine, $N(C_7H_7)_3$, and Di(1-cyclohepta-2,4,6-trienyl) amine, $NH(C_7H_7)_2$

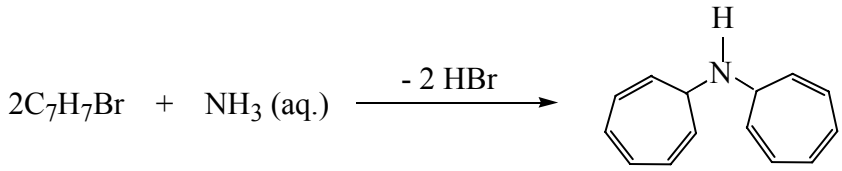
4.1 Synthesis of $N(C_7H_7)_3$ and $NH(C_7H_7)_2$

Tri(1-cyclohepta-2,4,6-trienyl) amine, $N(C_7H_7)_3$ (**24**), was first obtained by Doering and Knox in 1956 [12,132] by treatment of a cycloheptatrienylium bromide (tropylium bromide) suspension in diethyl ether with ammonia gas.



24

When aqueous ammonia was used instead of the gas ammonia, di(1-cyclohepta-2,4,6-trienyl) amine, $NH(C_7H_7)_2$ (**25**), was prepared successfully [12].



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NMR-Spectroscopic Characterization

The ^{1}H and ^{13}C NMR data of the cycloheptatrienyl amines **24** and **25** are summarized in Table 28 together with related compounds for comparison. From the proton NMR data of the different compounds, a small chemical shift variation is observed for proton H^1. Thus, $\delta(H^1)$ is 2.32 in tri(1-cyclohepta-2,4,6-trienyl) phosphane, 3.07 in tri(1-cyclohepta-2,4,6-trienyl) amine (**24**) and 3.03 in di(1-cyclohepta-2,4,6-trienyl) amine (**25**). The olefinic part (H^2-H^7) of the cyclohepta-

2,4,6-trienyl (C_7H_7) system shows little change. The ^1H spectra of $P(C_7H_7)_3$ and $N(C_7H_7)_3$ (**24**) consist of four different signals with an integral ratio 1:2:2:2. The spectrum of $NH(C_7H_7)_2$ consists of five different signals (*i.e.* 1 from the NH group and 4 from the cyclohepta-2,4,6-trienyl rings) with an integral ratio 1:2:4:4:4. The chemical shift of the proton at the 1-position of C_7H_8 was observed at higher magnetic field by more than 0.5 ppm compared with those at the corresponding position in $N(C_7H_7)_3$ (**24**) and $NH(C_7H_7)_2$ (**25**). In the ^{13}C NMR spectra, four different carbons are observed for the cycloheptatrienyl substituent. The signals of the C^1 atoms which connect directly to the N or P atoms are dramatically shifted upfield. In agreement with the "heavy atom effect", the chemical shift of C^1 changes from 58.3 ppm (for **24**) and 54.6 ppm (for **25**) to 36.1 ppm (for $P(C_7H_7)_3$).

Table 28. NMR data of C_7H_8, $P(C_7H_7)_3$, $N(C_7H_7)_3$ and $NH(C_7H_7)_2$ [a), b)]

	C_7H_8	$P(C_7H_7)_3$ [c)]	$N(C_7H_7)_3$ **24**	$NH(C_7H_7)_2$ **25**
^1H-NMR				
$\delta(H^1)$	2.24t (2H)	2.32dt (3H) [2.2], {7.2}	3.07t (3H)	3.03t (2H)
$\delta(H^2, H^7)$	5.36m (2H)	5.17m (6H)	5.52m (6H)	5.38m (4H)
$\delta(H^3, H^6)$	6.18m (2H)	6.19m (6H)	6.10m (6H)	6.16m (4H)
$\delta(H^4, H^5)$	6.58m (2H)	6.53m (6H)	6.61t (6H)	6.66m (4H)
δ(NH)				1.84s (1H)
^{13}C-NMR				
$\delta(C^1)$	28.0	36.1d [16.2]	58.3	54.6
$\delta(C^2, C^7)$	120.7	118.6d [11.7]	122.5	123.8
$\delta(C^3, C^6)$	126.6	126.7d [7.3]	127.1	126.2
$\delta(C^4, C^5)$	130.9	130.9s	130.9	130.9
^{14}N-NMR			-330.02	
^{31}P-NMR		-12.8		

a) NMR data in $CDCl_3$ at 25 °C.

b) NMR Multiplicities: s singlet, d doublet, t triplet, m multiplet.

c) Coupling constants in parentheses; [ ] coupling constants involving ^{31}P, { } J(H, H).

Molecular Structure of Tri(1-cyclohepta-2,4,6-trienyl) amine, $N(C_7H_7)_3$ (24)

The molecular structure and the numbering scheme are shown in Fig. 24; relevant bond distances and angles are given in Table 30.

The tertiary amine **24** crystallizes in the orthorhombic space group $P2_12_12_1$ with 4 molecules in the unit cell. In the crystal all cyclohepta-2,4,6-trienyl substituents have the boat conformation and are all connected to nitrogen in an equatorial position. Compared with the analogous tertiary phosphane, $P(C_7H_7)_3$, which contains the C_7H_7 substituents both in equatorial and in axial connection (ratio 2:1) [86], the amine **24** has a relatively flattened trigonal pyramid NC_3 with C-N-C angles of 116.7 ± 2° (av.) and N-C bond lengths of 145.9 pm (av.); the corresponding parameters for $P(C_7H_7)_3$ are C-P-C angles of 100.05 ± 3° (av.) and P-C bond lengths of 187.2 pm (av.) [86]. The sum of the angles around N and P, respectively, is 350.0° in $N(C_7H_7)_3$ (**24**) and 300.2° (av.) in $P(C_7H_7)_3$, the height of the pyramid (*i.e.* the distance of the heteratom from the C(1)C(8)C(15) plane) is 27.0 pm in $N(C_7H_7)_3$ (**24**), but 87.2 pm (av.) in $P(C_7H_7)_3$. The lone pair at N in $N(C_7H_7)_3$ (**24**) which is necessary for complexation is therefore less exposed than the lone pair at P in the versatile ligand $P(C_7H_7)_3$. Table 29 contains the height (h) of the pyramid in various derivatives of ammonia [133].

Table 29. Geometrical form of various amines

	NH_3	$N(CH_3)_3$	$N(C_6H_5)_3$	NFc_3	$N(C_7H_7)_3$	$P(C_7H_7)_3$ [86]	
					24	A	B
d(N-H) (pm)	101.5						
d(N-C) (pm)		145.1(3)	142(4)	141.4	145.9		
d(P-C) (pm)						187.3	187.1
< (HNH) (°)	106.6						
< (CNC) (°)		110.9(6)	116(2)	119.8	116.7		
< (CPC) (°)						100.4	99.7
h (pm) [a)]	38	45	23	6	27.0	86.4	87.9

a) The height (h) is the distance of the N or P atom from the plane of the three directly bonded neighboring atoms.

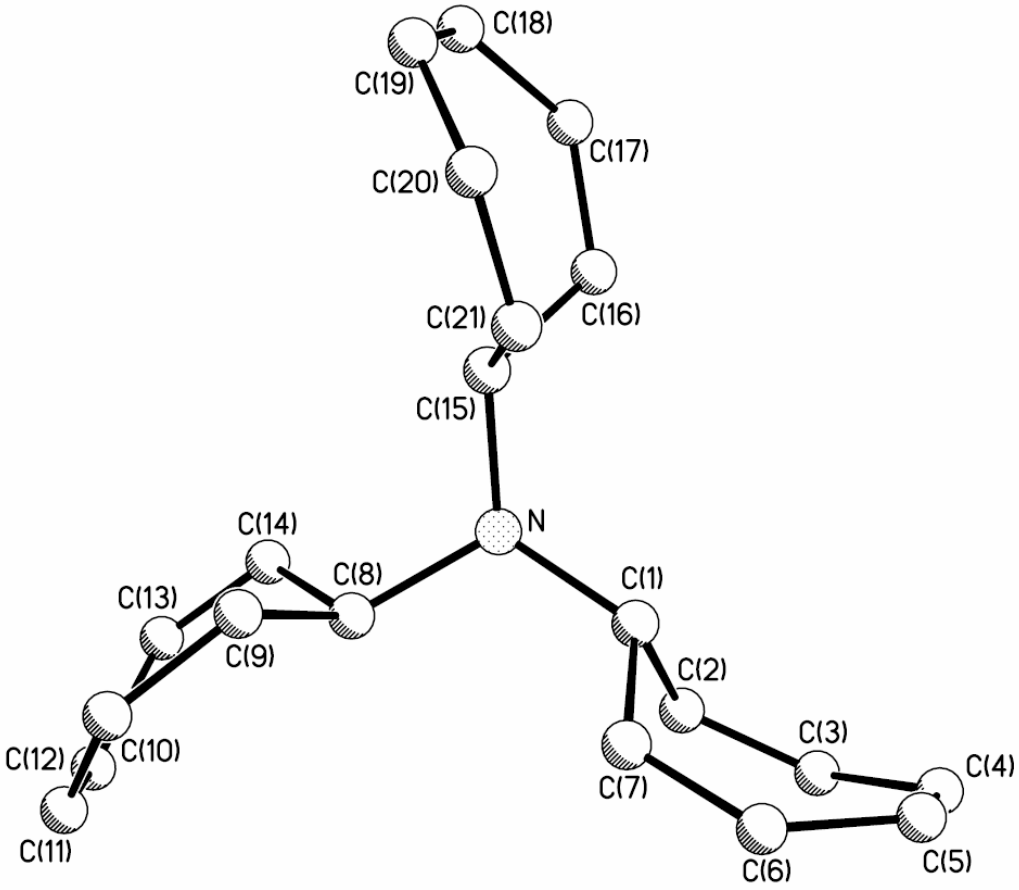


Fig.24. Molecular structure of tri(1-cyclohepta-2,4,6-trienyl) amine, $N(C_7H_7)_3$ (**24**)

The bond distances and bond angles of the three cyclohepta-2,4,6-trienyl substituents in $N(C_7H_7)_3$ (**24**) are comparable (Fig. 24), both among each other and with the corresponding values of the phosphane, $P(C_7H_7)_3$. The bending of the boat-shaped rings can be characterized by the dihedral angles α and β, which are defined in Fig. 2 in Chapter 2.

The parameters α = 54.2° (av.) and β = 26.5° (av.) in $N(C_7H_7)_3$ (**24**) have the typical values of equatorial C_7H_7 substituents (cf. α = 55.7° (av.) and β = 27.0° (av.) in $P(C_7H_7)_3$, α = 58.3° (av.) and β = 28.7° (av.) in $[P(C_7H_7)_4]BF_4$ [86]). Axial C_7H_7 substituents which are necessary for π-complexation have significantly smaller α and β parameters [86].

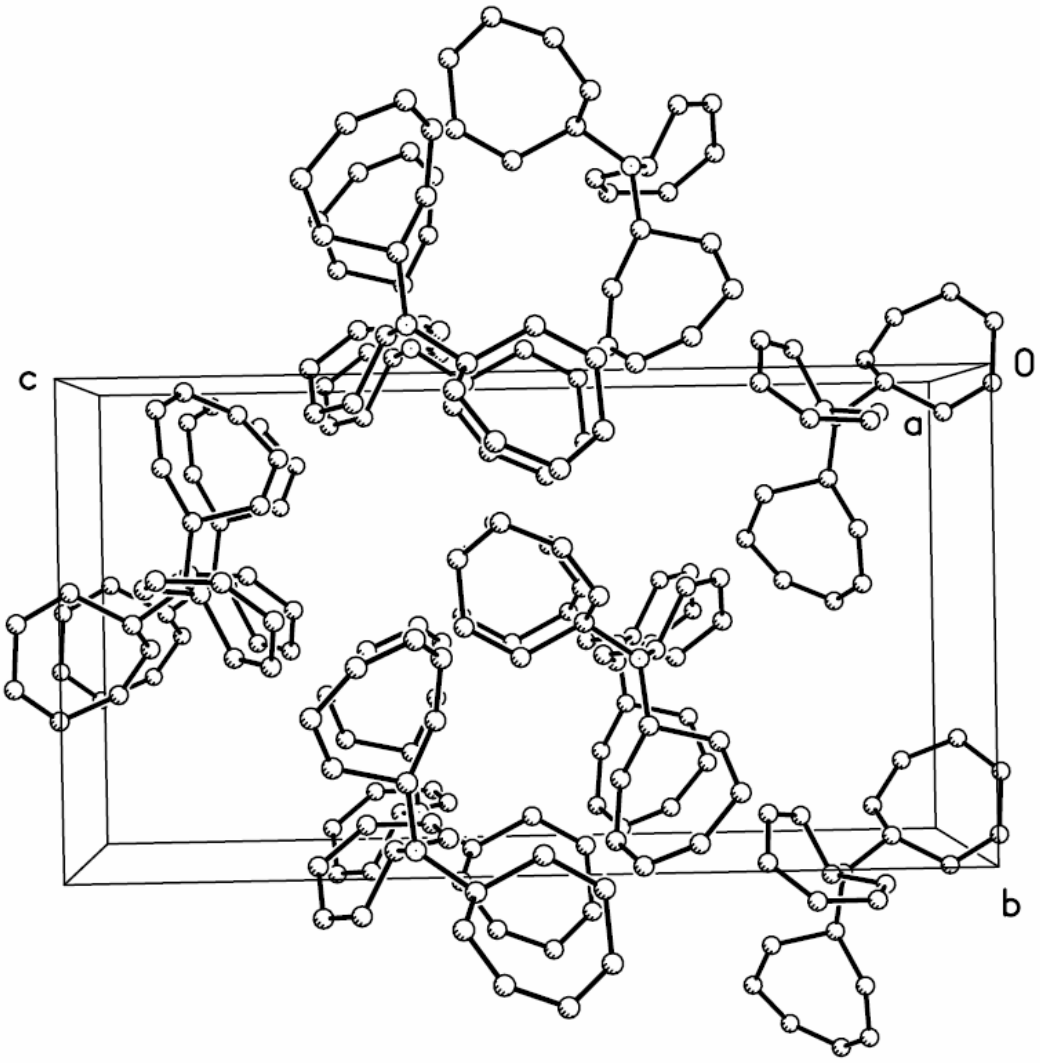


Fig.25. Packing diagram of tri(1-cyclohepta-2,4,6-trienyl) amine, $N(C_7H_7)_3$ (**24**)

The packing diagram (Fig. 25) shows the arrangement of the $N(C_7H_7)_3$ molecules in the crystal, which leads to the formation of channels along axis a.

Table 30. Atomic distances and angles of tri(1-cyclohepta-2,4,6-trienyl) amine, $N(C_7H_7)_3$ (24)

Bond lengths (pm)		Bond angles (°)	
N-C(1)	145.3(5)	C(1)-N-C(8)	116.1(3)
C(1)-C(2)	148.9(5)	N-C(1)-C(2)	110.9(4)
C(1)-C(7)	147.9(5)	N-C(1)-C(7)	117.5(4)
C(2)-C(3)	133.6(6)	C(2)-C(1)-C(7)	106.2(4)
C(3)-C(4)	143.5(7)	C(1)-C(2)-C(3)	122.6(5)
C(4)-C(5)	132.7(7)	C(2)-C(3)-C(4)	125.0(6)
C(5)-C(6)	143.0(7)	C(3)-C(4)-C(5)	124.6(7)
C(6)-C(7)	132.8(6)	C(4)-C(5)-C(6)	126.6(7)
N-C(8)	147.2(5)	C(5)-C(6)-C(7)	124.7(5)
C(8)-C(9)	149.5(5)	C(6)-C(7)-C(1)	123.1(5)
C(8)-C(14)	147.0(5)	C(8)-N-C(15)	115.1(4)
C(9)-C(10)	134.7(6)	N-C(8)-C(9)	116.6(4)
C(10)-C(11)	143.2(6)	N-C(8)-C(14)	111.5(4)
C(11)-C(12)	133.0(7)	C(9)-C(8)-C(14)	106.9(4)
C(12)-C(13)	140.5(6)	C(8)-C(9)-C(10)	120.6(5)
C(13)-C(14)	133.0(6)	C(9)-C(10)-C(11)	125.7(5)
N-C(15)	145.3(4)	C(10)-C(11)-C(12)	125.0(5)
C(15)-C(16)	149.6(5)	C(11)-C(12)-C(13)	126.6(6)
C(15)-C(21)	150.4(5)	C(12)-C(13)-C(14)	124.8(5)
C(16)-C(17)	133.8(6)	C(13)-C(14)-C(8)	122.4(5)
C(17)-C(18)	142.2(7)	C(1)-N-C(15)	118.8(4)
C(18)-C(19)	134.8(6)	N-C(15)-C(16)	112.1(4)
C(19)-C(20)	142.5(6)	N-C(15)-C(21)	118.0(4)
C(20)-C(21)	133.7(5)	C(16)-C(15)-C(21)	105.3(3)
		C(15)-C(16)-C(17)	120.6(5)
Dihedral angles (°) [a)]		C(16)-C(17)-C(18)	124.8(5)
α_1 / β_1	52.5 / 26.6	C(17)-C(18)-C(19)	125.8(5)
α_8 / β_8	54.2 / 25.8	C(18)-C(19)-C(20)	125.0(5)
α_{15} / β_{15}	55.8 / 27.2	C(19)-C(20)-C(21)	125.2(5)
		C(20)-C(21)-C(15)	121.2(4)

a) The numbering of the dihedral angles α and β (Fig. 2) for the 3 cyclohepta-2,4,6-trienyl substituents refer to the N-bonded carbon atom.

The diffraction data and the refinement parameters for **24**, calculated from the X-ray structure analysis, are shown in Table 31.

Table 31. Crystal data and structure refinement for 24

Empirical formula	$C_{21}\ H_{21}\ N$
Formula weight	287.39
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 8.9911(18) Å α = 90°
	b = 10.103(2) Å β = 90°
	c = 18.735(4) Å γ = 90°
Volume	1701.8(6) $Å^3$
Z	4
Density (calculated)	1.122 Mg/m^3
Absorption coefficient	0.064 mm^{-1}
F(000)	616
Crystal size	0.16 x 0.14 x 0.06 mm^3
θ range for data collection	2.17 to 26.18°
Index ranges	-11<h<11, -12<k<12, -23<l<23
Reflections collected	13400
Independent reflections	3351 [R(int) = 0.1150]
Completeness to θ = 24.99°	98.7 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3351 / 0 / 199
Goodness-of-fit on F^2	0.626
Final R indices [I > 2σ (I)]	R1 = 0.0412, wR2 = 0.0676
R indices (all data)	R1 = 0.1907, wR2 = 0.1016
Absolute structure parameter	-8(8)
Largest diff. peak and hole	0.188 and -0.082 e.$Å^{-3}$

4.2 Diels-Alder Reactions of $N(C_7H_7)_3$ and $NH(C_7H_7)_2$

In Chapter 2 the Diels-Alder reactions of di(1-cyclohepta-2,4,6-trienyl) thioether, $S(C_7H_7)_2$ (**1**), with maleic anhydride, maleimide and N-phenyl maleimide have been discussed. The products **4a**, **4b** and **4c** had been obtained, in which one cyclohepta-2,4,6-trienyl ring was unchanged and the other ring had been modified by the Diels-Alder reaction.

When tri(1-cyclohepta-2,4,6-trienyl) amine, $N(C_7H_7)_3$ (**24**), and di(1-cyclohepta-2,4,6-trienyl) amine, $NH(C_7H_7)_2$ (**25**), were used as the starting materials, the expected Diels-Alder products with maleic anhydride (**26a** and **27a**) could not be isolated. The reactions gave new products, which, however, could not be identified from the ^{1}H NMR, ^{13}C NMR and EI mass spectra. However, refluxing tri(1-cyclohepta-2,4,6-trienyl) amine, $N(C_7H_7)_3$ (**24**), or di(1-cyclohepta-2,4,6-trienyl) amine, $NH(C_7H_7)_2$ (**25**), in THF solution in the presence of maleimide and N-phenyl maleimide led to the expected Diels-Alder reactions (Fig. 26 and Fig. 27).

When the ratio of maleimide to $N(C_7H_7)_3$ (**24**) was 3:1, the product **26b** was obtained and isolated as white crystals. In **26b** two cyclohepta-2,4,6-trienyl rings were unchanged and only one ring had been involved in the Diels-Alder reaction. Under the same reaction conditions, $N(C_7H_7)_3$ (**24**) reacted with N-phenyl maleimide to give **26c**, where one cyclohepta-2,4,6-trienyl ring was unchanged and two rings had been involved in the Diels-Alder reaction. The composition and the structure of the new products **26b** and **26c** were deduced from the ^{1}H and ^{13}C NMR spectra, supported by the EI-mass spectra.

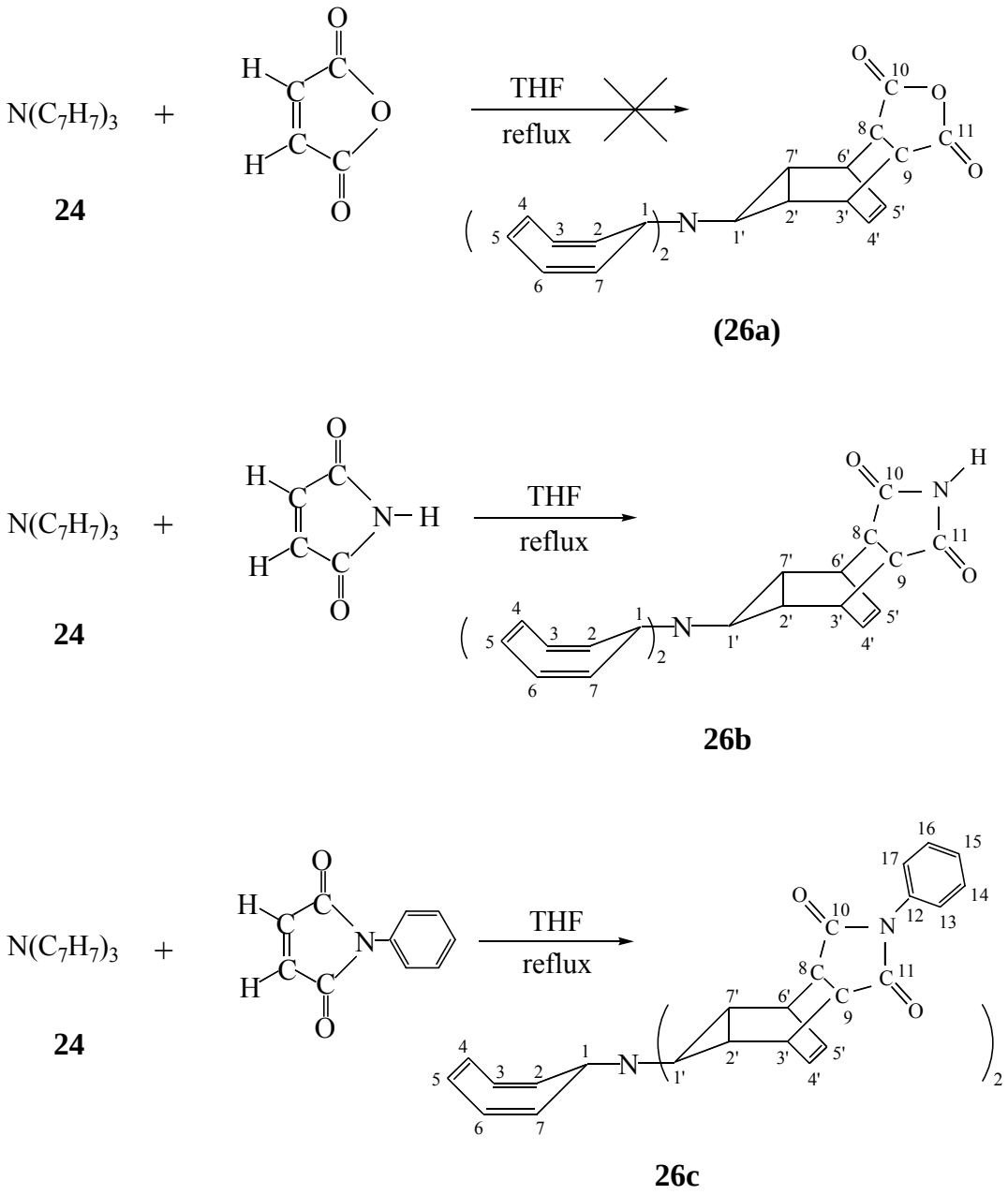


Fig.26. Synthesis of the Diels-Alder adducts **26b** and **26c**

Di(1-cyclohepta-2,4,6-trienyl) amine, $NH(C_7H_7)_2$ (**25**), reacted with maleimide and N-phenyl maleimide to give **27b** and **27c**, in which one cyclohepta-2,4,6-trienyl ring was unchanged and the other ring had been involved in the Diels-Alder reaction.

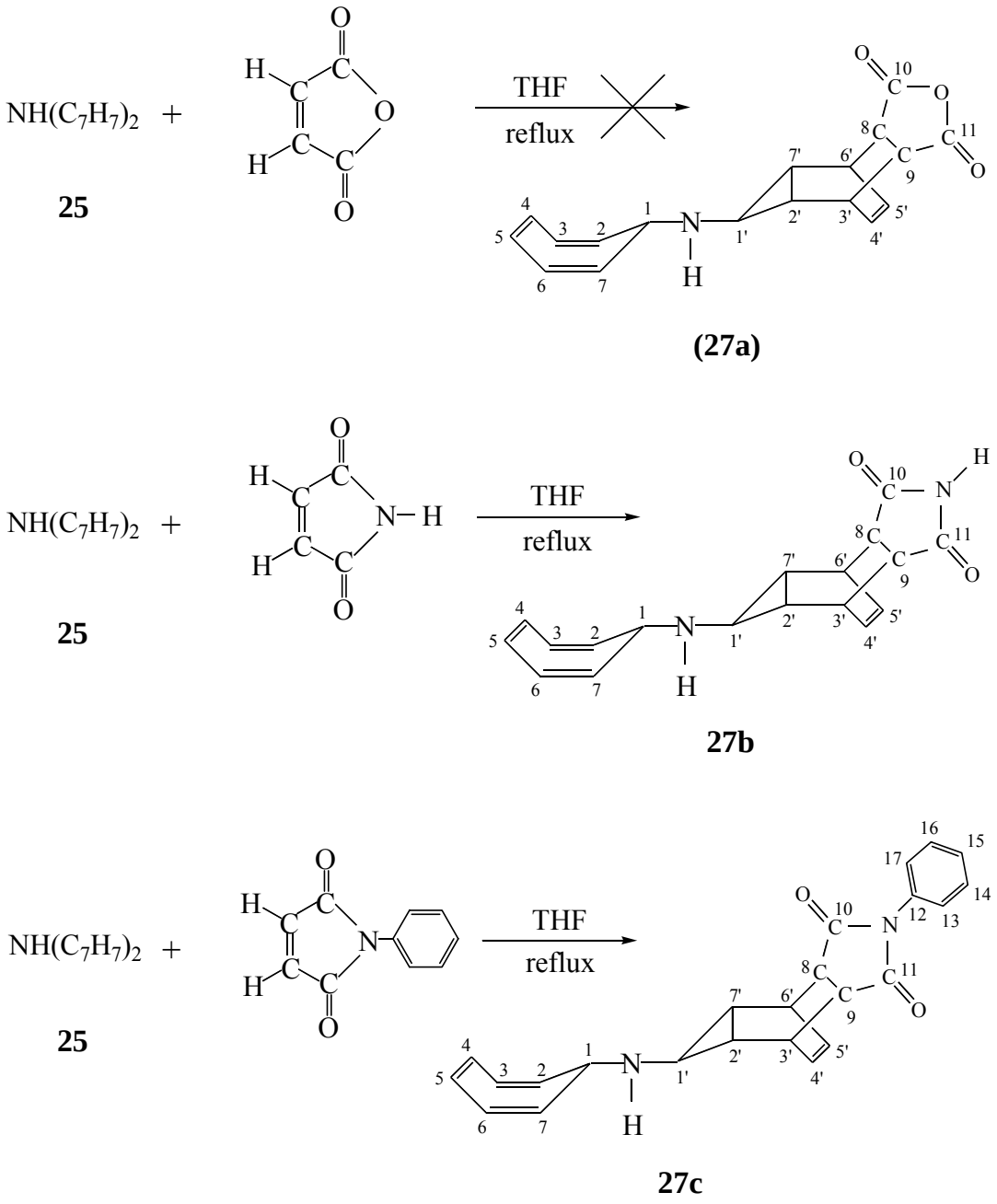


Fig.27. Synthesis of the Diels-Alder adducts **27b** and **27c**

NMR-Spectroscopic Characterization

For the addition compound **26b**, a total of ten ^{1}H NMR signals (*i.e.* 4 originating from two unchanged cyclohepta-2,4,6-trienyl rings, 4 from the reacted ring and 2 from the maleimide unit) and ten ^{13}C NMR signals are observed (Table 32).

From the ^1H NMR and ^{13}C NMR spectra of **26b** and **26c**, it is indicated that Diels-Alder reactions take place when tri(1-cyclohepta-2,4,6-trienyl) amine (**24**) reacts with maleimide and N-phenyl maleimide. The spectra of the products are very similar, except that the integrals of the signals are different and the product **26c** contains the extra signals of the phenyl group. For compound **26b** the ratio of the integral of cyclohepta-2,4,6-trienyl ring to that of the changed ring is 14:7. This indicated that two cycloheptatrienyl rings were unchanged and only one ring had reacted. However, for compound **26c** the ratio of the integrals is 7:14, illustrating that one cycloheptatrienyl ring had remained unchanged and the other two rings were involved in the Diels-Alder reaction. For the unreacted cycloheptatrienyl ring, chemical shifts of the protons show a slight variation compared with those at the corresponding positions of tri(1-cyclohepta-2,4,6-trienyl) amine (**24**). The substituted ring has changed to the norcaradienyl structure with a triangle attached to the nitrogen atom. This can be seen particularly from the high-field shift of the signals assigned to the "aliphatic" positions $H^{1'}$, $H^{2'}$ and $H^{7'}$. The protons of $H^{3'}$, $H^{6'}$ and H^8, H^9 also shift to higher magnetic field because new bonds were formed between the carbons of $C^{3'}$, $C^{6'}$ and C^8, C^9. In addition, the chemical shifts of $H^{4'}$ and $H^{5'}$ also changed to higher magnetic field due to the disappearance of the double bonds between $C^{2'}$, $C^{3'}$ and $C^{6'}$, $C^{7'}$. In the carbon NMR spectra the same effects were observed. This provides strong evidence that the Diels-Alder reactions took place in the expected way.

Table 32. NMR data of the Diels-Alder adducts 26b and 26c (cf. Fig. 26) [a), b)]

	26b	**26c**
^1H-NMR		
$\delta(H^1)$	3.42t (2H)	3.54t (1H)
$\delta(H^2, H^7)$	5.53m, 5.42m (4H)	5.58m (2H)
$\delta(H^3, H^6)$	6.16m (4H)	6.14m (2H)
$\delta(H^4, H^5)$	6.57t (4H)	6.60t (2H)
$\delta(H^{1'})$	1.80t (1H)	1.60t (2H)
$\delta(H^{2'}, H^{7'})$	1.27t (2H)	1.24t (4H)
$\delta(H^{3'}, H^{6'})$	3.42m (2H)	3.54m (4H)
$\delta(H^{4'}, H^{5'})$	5.82m (2H)	5.89m (4H)
$\delta(H^8, H^9)$	2.94t (2H)	3.08t (4H)
δ(NH)	7.75br (1H)	
δ(NPh)		7.41-7.33m, 7.15-7.11m (10H)

^{13}C-NMR		
$\delta(C^1)$	40.2	40.0
$\delta(C^2, C^7)$	124.2	123.3
$\delta(C^3, C^6)$	128.7	124.2
$\delta(C^4, C^5)$	135.1	130.8
$\delta(C^{1'})$	15.3	15.2
$\delta(C^{2'}, C^{7'})$	18.4	17.1
$\delta(C^{3'}, C^{6'})$	32.3	32.7
$\delta(C^{4'}, C^{5'})$	130.8	128.7
$\delta(C^8, C^9)$	46.1	44.7
$\delta(C^{10}, C^{11})$	178.1	177.0
$\delta(C^{12})$		131.7
$\delta(C^{13}, C^{17})$		129.0
$\delta(C^{14}, C^{16})$		126.3
$\delta(C^{15})$		128.5

a) NMR data in $CDCl_3$ at 25 °C.

b) NMR Multiplicities: s singlet, t triplet, m multiplet, br broad.

The ^{1}H NMR and ^{13}C NMR spectra of the products **27b** and **27c** showed that Diels-Alder reactions took place when di(1-cyclohepta-2,4,6-trienyl) amine (**25**) reacted with maleimide and N-phenyl maleimide. The spectra of the compounds **27b** and **27c** are similar to those of the compounds **4b** and **4c** which were shown in Chapter 2 except that there is another signal for the hydrogen which is connected to the central nitrogen atom. The spectra indicated that one cycloheptatrienyl ring was unchanged and the other ring had reacted (Table 33).

Table 33. NMR data of the Diels-Alder adducts 27b and 27c (cf. Fig. 27) [a), b)]

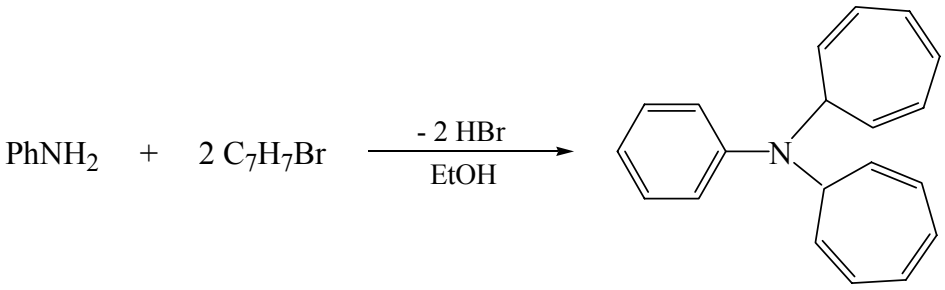
	27b	**27c**
^{1}H-NMR		
$\delta(H^1)$	3.42t (1H)	3.46t (1H)
$\delta(H^2, H^7)$	5.39m (2H)	5.33m (2H)
$\delta(H^3, H^6)$	6.14m (2H)	6.10m (2H)
$\delta(H^4, H^5)$	6.65t (2H)	6.61t (2H)
$\delta(H^{1'})$	1.92s (1H)	1.55t (1H)
$\delta(H^{2'}, H^{7'})$	1.21t (2H)	1.17t (2H)
$\delta(H^{3'}, H^{6'})$	2.96m (2H)	2.98m (2H)
$\delta(H^{4'}, H^{5'})$	5.82m (2H)	5.83m (2H)
$\delta(H^8, H^9)$	3.42t (2H)	3.46t (2H)
δ(NH)(in maleimide)	7.80br (1H)	
δ(NPh)		7.27-7.40m (5H)
δ(NH)	1.92s (1H)	1.91s (1H)
^{13}C-NMR		
$\delta(C^1)$	54.4	54.3
$\delta(C^2, C^7)$	124.0	123.4
$\delta(C^3, C^6)$	125.8	126.1
$\delta(C^4, C^5)$	130.9	130.5
$\delta(C^{1'})$	34.9	34.4
$\delta(C^{2'}, C^{7'})$	18.7	18.7
$\delta(C^{3'}, C^{6'})$	32.4	32.5
$\delta(C^{4'}, C^{5'})$	128.7	128.6
$\delta(C^8, C^9)$	46.0	44.4
$\delta(C^{10}, C^{11})$	170.7	176.8
$\delta(C^{12})$		130.5
$\delta(C^{13}, C^{17})$		125.7
$\delta(C^{14}, C^{16})$		128.7
$\delta(C^{15})$		127.5

a) NMR data in $CDCl_3$ at 25 °C.

b) NMR Multiplicities: s singlet, t triplet, m multiplet, br broad.

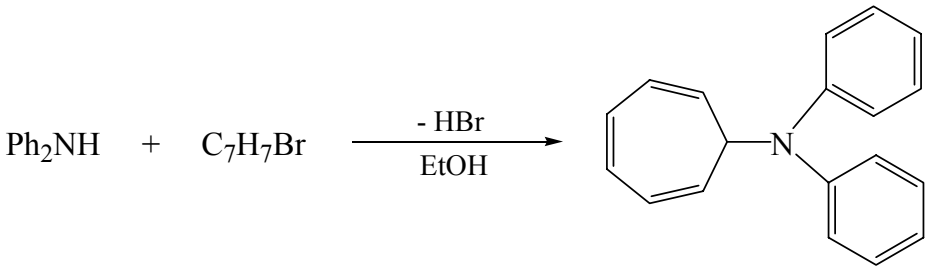
4.3 Synthesis of $N(Ph)(C_7H_7)_2$ and $N(Ph)_2(C_7H_7)$

In analogy to the preparations of tri(1-cyclohepta-2,4,6-trienyl) amine, $N(C_7H_7)_3$ (**24**), and di(1-cyclohepta-2,4,6-trienyl) amine, $NH(C_7H_7)_2$ (**25**), we originally used diethyl ether or water as the solvent to prepare di(1-cyclohepta-2,4,6-trienyl)phenylamine, $N(Ph)(C_7H_7)_2$ (**28**), and (1-cyclohepta-2,4,6-trienyl)diphenylamine, $N(Ph)_2(C_7H_7)$ (**29**), but the syntheses were not successful, possibly due to the insolubility of C_7H_7Br in ether and the insolubility of $PhNH_2$ and Ph_2NH in water. Therefore, we used ethanol as the solvent. When the ratio of tropylium bromide (C_7H_7Br) to aniline ($PhNH_2$) is 2:1, the tertiary amine $N(Ph)(C_7H_7)_2$ (**28**) is obtained as yellow solid.



28

In addition, tropylium bromide (C_7H_7Br) reacted with diphenylamine (Ph_2NH) to provide $N(Ph)_2(C_7H_7)$ (**29**) which was crystallized from ethanol as light-blue solid.



29

NMR-Spectroscopic Characterization

The ^1H and ^{13}C NMR data of the compounds $N(Ph)(C_7H_7)_2$ (**28**) and $N(Ph)_2(C_7H_7)$ (**29**) are summarized in Table 34. The ^1H NMR spectra of these two compounds consist of four signals with an integral ratio of 1:2:2:2 for the cycloheptatrienyl group and several overlapping signals in the range 7-8 ppm for the phenyl group. The chemical shift of the proton at the 1-position of cycloheptatrienyl group was observed

at a little higher magnetic field compared with those at the corresponding position of $N(C_7H_7)_3$ (**24**) and $NH(C_7H_7)_2$ (**25**). In the ^{13}C NMR spectra, four different carbons are observed from the cycloheptatrienyl substituent and another four carbon signals from the phenyl group. From the ratio of the integrals of the cyclohepta-2,4,6-trienyl ring to that of the phenyl group as well as from the results of the EI-MS, the composition of the compounds **28** and **29** is unequivocally determined. The assignments in Table 34 are supported by heteronuclear $^{1}H/^{13}C$ correlation spectra.

Table 34. NMR data of $N(Ph)(C_7H_7)_2$ (28) and $N(Ph)_2(C_7H_7)$ (29) [a), b)]

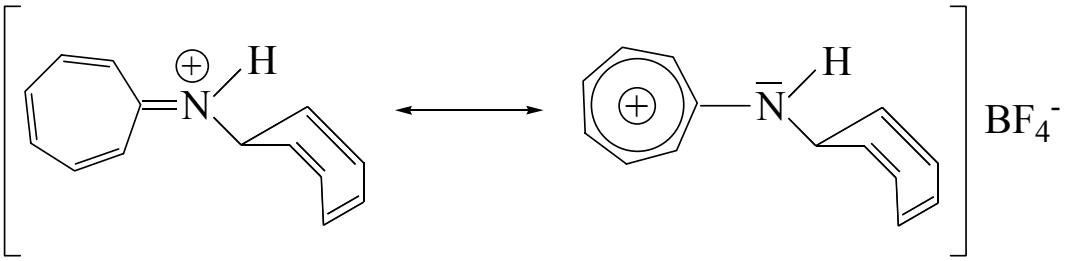
	$N(Ph)(C_7H_7)_2$ **28**	$N(Ph)_2(C_7H_7)$ **29**
^{1}H-NMR		
$\delta(H^1)$	2.79t (2H)	2.70t (1H)
$\delta(H^2, H^7)$	5.37dd (4H)	5.36m (2H)
$\delta(H^3, H^6)$	6.27m (4H)	6.24m (2H)
$\delta(H^4, H^5)$	6.72t (4H)	6.73t (2H)
δ(Ph)	7.41-7.60m (5H)	7.31-7.42m (10H)
^{13}C-NMR		
$\delta(C^1)$	44.7	44.7
$\delta(C^2, C^7)$	125.2	125.8
$\delta(C^3, C^6)$	125.0	124.6
$\delta(C^4, C^5)$	131.1	131.0
	123.7(o)	128.9(o)
δ(Ph)	129.2(m); 122.7(p)	138.3(m); 121.0(p)
	145.4(i)	141.1(i)

a) NMR data in $CDCl_3$ at 25 °C.

b) NMR Multiplicities: s singlet, dd doublet of doublets, t triplet, m multiplet.

4.4 Reaction of $N(C_7H_7)_3$ with $[C_7H_7]BF_4$

Whereas tri(1-cyclohepta-2,4,6-trienyl) phosphane, $P(C_7H_7)_3$, reacts with tropylium tetrafluoroborate, $[C_7H_7]BF_4$, in tetrahydrofuran or dichloromethane solution to give the phosphonium salt $[P(C_7H_7)_4]BF_4$ in quantitative yield [86], the corresponding reaction of $N(C_7H_7)_3$ (**24**) with $[C_7H_7]BF_4$ (1:1) leads to the N-tropylidene-N-(1-cyclohepta-2,4,6-trienyl)-immonium tetrafluoroborate salt, $[(C_7H_6)N(H)(C_7H_7)]BF_4$ (**30**), for which two canonical structures (**30'** and **30''**) can be formulated [134]:



(**30'**) (**30"**)

30

The use of $[C_7H_7]BF_4$ for the abstraction of a hydride ion from (1-cyclohepta-2,4,6-trienyl) amines, (C_7H_7)-N(R)(R') (R = R' = Me, Et; R = H, R' = Me, Pr, C_7H_7) had been described earlier [134,135], and **30** had been obtained [134] with $NH(C_7H_7)_2$ (**25**) as the educt. The formation of the secondary amine derivative **30** from the reaction of $N(C_7H_7)_3$ (**24**) with $[C_7H_7]BF_4$ can be ascribed to the facile hydrolytic splitting of N-C_7H_7 bonds. Thus, $N(C_7H_7)_3$ (**24**) dissolves easily in diluted acids such as HCl and HBF_4 to give tropylium salts, as shown by the characteristic singlet of the tropylium ion, $[C_7H_7^+]$, in the ^1H and ^{13}C NMR spectra, e.g. $\delta(^1H) = 9.2$ and $\delta(^{13}C) = 155.4$ (in D_2O), after treatment of **24** with diluted HBF_4 acid.

The ^1H and ^{13}C NMR spectra (Table 35) clearly demonstrate that the products **30** obtained from the reactions of either $N(C_7H_7)_3$ (**24**) or $NH(C_7H_7)_2$ (**25**) with $[C_7H_7]BF_4$ are essentially identical.

Table 35. NMR data of compound 30 [a)]

	$[(C_7H_6)N(H)(C_7H_7)]^+BF_4^-$ (**30**)	
	A [b)]	**B** [b)]
^{1}H-NMR		
$\delta(H^1)$	3.72t (1H)	3.74br (1H)
$\delta(H^2, H^7)$	5.57m (2H)	5.57m (2H)
$\delta(H^3, H^6)$	6.42m (2H)	6.43m (2H)
$\delta(H^4, H^5)$	6.89t (2H)	6.88m (2H)
δ(NH)	9.45br (1H)	9.34br (1H)
$\delta(C_7H_6^+)$	7.32m, 7.63-7.95m (6H)	7.28/7.32m, 7.63-7.89m (6H)
^{13}C-NMR		
$\delta(C^1)$	55.1	54.9
$\delta(C^2, C^7)$	120.1	120.0
$\delta(C^3, C^6)$	126.5	126.5
$\delta(C^4, C^5)$	132.2	132.2
$\delta(C_7H_6^+)$ [c)]	128.3, 136.3, 139.4, 141.8, 144.2, 147.1, 166.8	128.3, 136.1, 139.6, 141.8, 144.2, 147.2, 166.8
^{11}B-NMR	2.14	2.14q [*J*(B, F) 1.0 Hz]

a) The tetrafluoroborate **30** was measured in CD_2Cl_2 at 25 °C.

b) **A** was obtained by the reaction of **24** with $[C_7H_7]BF_4$ in CH_2Cl_2, **B** by the reaction of **25** with $[C_7H_7]BF_4$ in CH_2Cl_2.

c) For comparison: $[C_7H_7]Br$: $\delta(^1H)$ 9.20s; $\delta(^{13}C)$ 155.4 (in D_2O);
$[C_7H_7]BF_4$: $\delta(^1H)$ 9.17s; $\delta(^{13}C)$ 155.3; $\delta(^{11}B)$ 1.59 (in D_2O).

In both cases the NMR spectra indicate the presence of a normal (bent) 1-cyclohepta-2,4,6-trienyl substituent (as in $N(C_7H_7)_3$ (**24**) and $NH(C_7H_7)_2$ (**25**)) and a "more aromatic" seven-membered ring system. The observation of 7 different ^{13}C NMR signals for the "aromatic" ring (Fig. 28) can be rationalized on the assumption that the rotation around the N-C(8) bond is restricted due to partial double bond character.

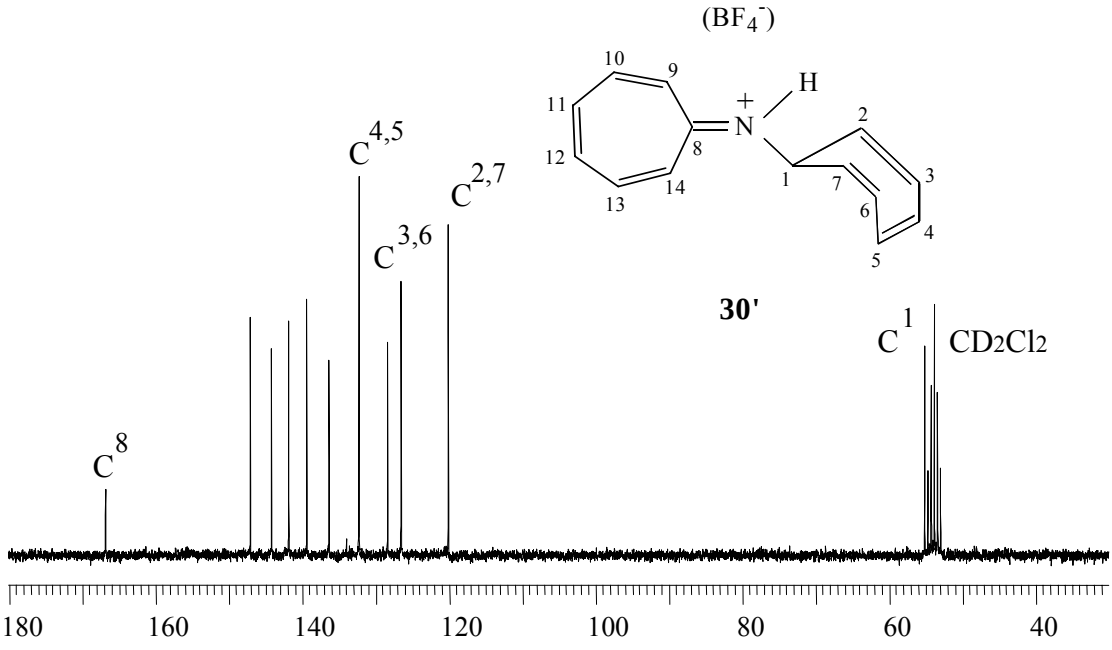


Fig.28. ^{13}C NMR spectrum of compound **30**

The N-H group in **30** is indicated by a broad ^1H NMR signal ($\delta(^1H)$ = 9.44 in CD_2Cl_2 solution) and a broadened absorption (ν(N-H) = 3277 cm^{-1}) in the IR solution spectra (CH_2Cl_2), although the corresponding band was not observed using CsI pellets.

A preliminary X-ray structure analysis of **30** (which suffers from severe disorder, in particular of the BF_4^- anions) leads to the conclusion that the cation is best described by the amino-substituted tropylium structure **30'** (cf. [134]) (Fig. 29). It is known that alkylamino substituents increase the stability of tropylium ions [136,137].

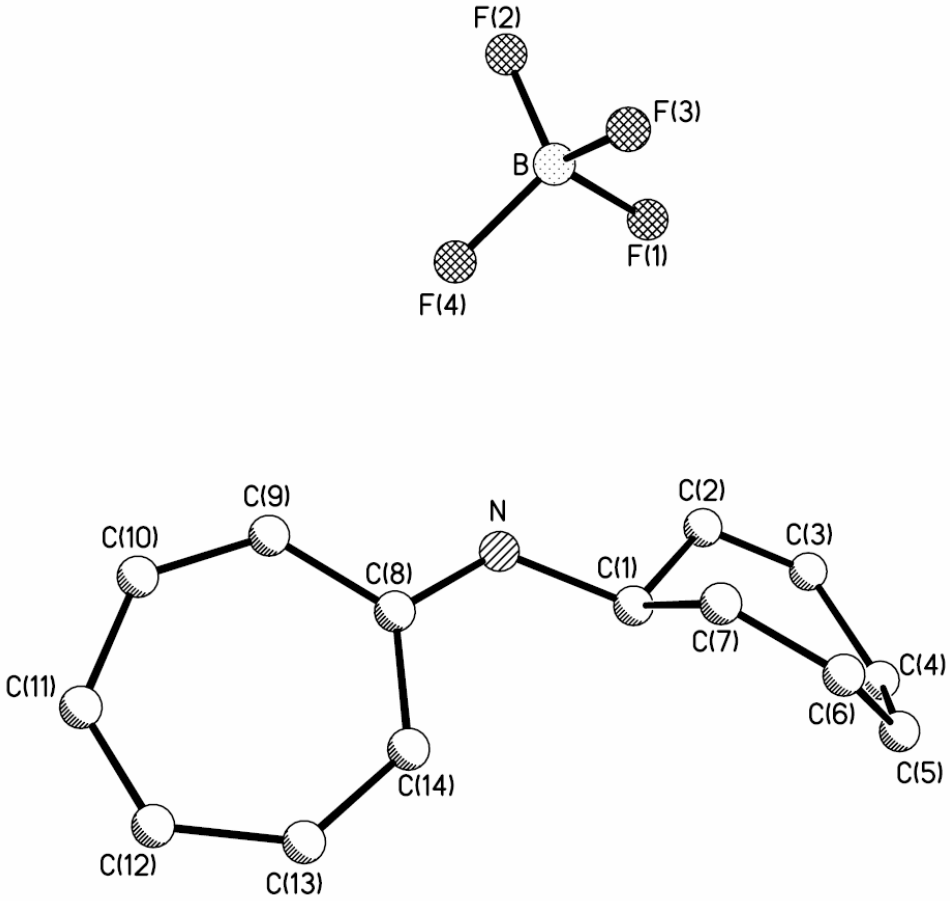


Fig.29. Molecular structure of compound **30**

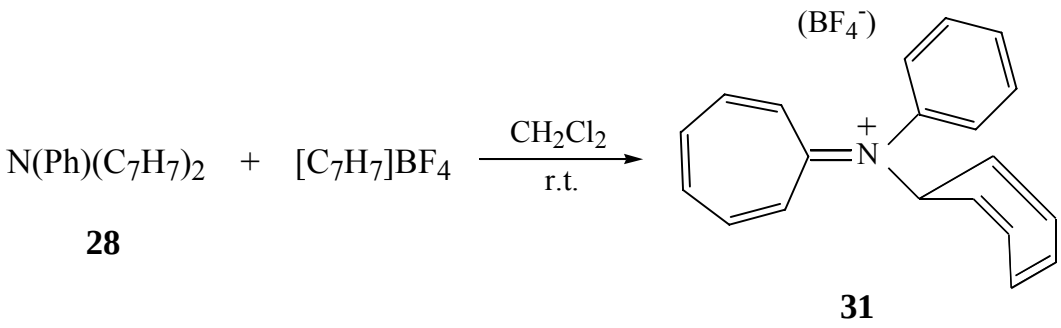
The (1-cyclohepta-2,4,6-trienyl)amino substituent in the cation of **30** corresponds to the geometry found in $N(C_7H_7)_3$ (**24**) with an equatorial attachment of the boat-shaped seven-membered ring to nitrogen (α = 56.9°, β = 25.9°, N-C(1) 146.9(7) pm). The angle C(1)-N-C(8) (126.8(4)°) is also in the range expected for a flat pyramid; however, the hydrogen atom attached to the central nitrogen could not be located. The N-C(8) bond (130.9(6) pm) indicates some multiple bond character, the calculated bond lengths are 147 pm for the C-N single and 122 pm for the C=N double bond [138].

At first sight, the tropylium ring (C(8)-C(14)) appears to be nearly planar (with an average deviation of the carbon atom of Δ = 3.5 pm), and the C(8)=N bond protrudes by an angle of 6.1° from this plane. However, the cationic ring is actually present in a very shallow boat conformation (with α = 7.4° and β = 3.6°). This form had been observed earlier for the salt $[O(C_7H_6)_2](CF_3SO_3)_2$ [89] containing an ether dication in which two substituted tropylium rings ($C_7H_6^+$) are connected through an oxo bridge. Comparable with the situation in **30**, the dication $[O(C_7H_6)_2]^{2+}$ contains a bent C-O-C

system (125.3(4)°) and shortened C-O bond lengths (135.6(3) pm), the calculated values are 143 pm for the C-O single bond and 119 pm for the C=O double bond [138]. The very shallow boat conformation appears to be also characteristic of tropone and simple tropone derivatives [89].

4.5 Reaction of $N(Ph)(C_7H_7)_2$ with $[C_7H_7]BF_4$

As expected, the tertiary amine $N(Ph)(C_7H_7)_2$ (**28**) reacted with $[C_7H_7]BF_4$ and provided the dark-red salt $[(C_7H_6)N(Ph)(C_7H_7)]^+BF_4^-$ (**31**), in which one cyclohepta-2,4,6-trienyl ring is attached to the nitrogen in the boat conformation, and another tropylium ring connected to the nitrogen is nearly planar. Compared with compound **30**, the third position at the nitrogen atom in compound **31** is occupied by a phenyl group.



28 **31**

NMR-Spectroscopic Characterization

The ^1H and ^{13}C NMR data of the salt **31** are shown in Table 36. The spectrum of **31** is very similar to that of **30**, except that compound **31** contains the extra signals of the phenyl group. The chemical shift of H^1 in the cyclohepta-2,4,6-trienyl ring of **31** is observed at higher magnetic field by nearly 1 ppm compared with that at the corresponding position of compound **30**. The ^{13}C NMR spectra of **31** show 15 signals totally which include 4 signals from the boat-shaped cyclohepta-2,4,6-trienyl substituent, 7 signals from the "aromatic" ring and 4 signals from the phenyl group.

Table 36. NMR data of compound 31 [a)]

$[(C_7H_6)N(Ph)(C_7H_7)]^+BF_4^-$ (**31**)			
^{1}H-NMR		^{13}C-NMR	
$\delta(H^1)$	2.85t (1H)	$\delta(C^1)$	45.2
$\delta(H^2, H^7)$	5.42m (2H)	$\delta(C^2, C^7)$	125.2
$\delta(H^3, H^6)$	6.28m (2H)	$\delta(C^3, C^6)$	125.3
$\delta(H^4, H^5)$	6.76m (2H)	$\delta(C^4, C^5)$	131.4
δ(Ph) [b)]	7.40-7.74m (11H)	δ(Ph) [b)]	124.9 (o) 130.0 (m); 133.6 (p) 146.3 (i)
$\delta(C_7H_6^+)$		$\delta(C_7H_6^+)$	129.3, 136.4, 140.6, 141.8, 145.1, 146.7, 166.6

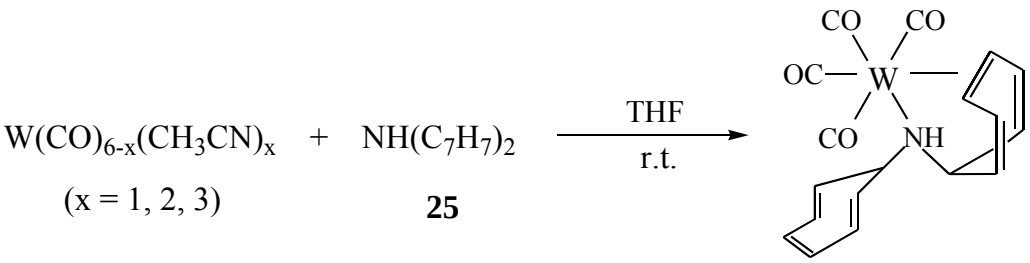
a) The tetrafluoroborate **31** was measured in CD_2Cl_2 at 25 °C.

b) For comparison: NPh_3: $\delta(^1H)$ 6.97 (1H), 7.13 (2H), 7.23 (2H);
$\delta(^{13}C)$ 122.6(p), 124.1(o), 129.1(m), 147.8(i) (in $CDCl_3$).

4.6 Preparation of Complex $W(CO)_4[(\eta^2\text{-}C_7H_7)NH(C_7H_7)]$

Attempts to use the amine $N(C_7H_7)_3$ (**24**) in a similar manner as $P(C_7H_7)_3$ as a ligand in transition metal complexes were essentially unsuccessful. Although interactions of **24** with the metal complex were occasionally indicated by color effects, no defined products could be isolated. The missing tendency of $N(C_7H_7)_3$ (**24**) towards coordination was tentatively ascribed to its molecular structure which is described above.

In addition, attempts to use the amine $NH(C_7H_7)_2$ (**25**) as a ligand in coordination chemistry were also carried out. But, most experiments were not successful. Fortunately, when reacting **25** with the mixture of carbonyl(acetonitrile) tungsten complexes, $W(CH_3CN)_x(CO)_{6-x}$ (x = 1, 2, 3), the tetracarbonyl tungsten complex $W(CO)_4[NH(\eta^2\text{-}C_7H_7)(C_7H_7)]$ (**32**) was obtained, in which one cyclohepta-2,4,6-trienyl substituent appears to be coordinated to the metal through its central double bond and the other seven-membered ring is freely pending. A single crystal of **32** could not be obtained. Therefore, its structural characterization is based on the ^{1}H and ^{13}C NMR spectra, together with the pattern of the carbonyl stretching absorption in the IR spectra and the result of the EI mass spectrometry.



32

IR and NMR Spectroscopy

Table 37 contains the IR stretching frequencies of the carbonyl ligands (in pentane solution) and the ^1H and ^{13}C NMR data (in $CDCl_3$ solution) of complex **32**.

Table 37. NMR spectroscopic data of the complex 32 [a)]

$W(CO)_4[(\eta^2\text{-}C_7H_7)NH(C_7H_7)]$ (**32**)			
^1H-NMR		^{13}C-NMR	
$\delta(H^1)$	3.69 (1H)	$\delta(C^1)$	61.2
$\delta(H^2, H^7)$	5.58 (2H)	$\delta(C^2, C^7)$	123.4
$\delta(H^3, H^6)$	6.42 (2H)	$\delta(C^3, C^6)$	127.7
$\delta(H^4, H^5)$	6.64 (2H)	$\delta(C^4, C^5)$	130.7
$\delta(H^{1'})$	4.29 (1H)	$\delta(C^{1'})$	77.2
$\delta(H^{2'}, H^{7'})$	5.58 (2H)	$\delta(C^{2'}, C^{7'})$	123.4
$\delta(H^{3'}, H^{6'})$	6.64 (2H)	$\delta(C^{3'}, C^{6'})$	130.7
$\delta(H^{4'}, H^{5'})$	5.58 (2H)	$\delta(C^{4'}, C^{5'})$	123.4
δ(NH)	1.88 (1H)	δ(CO)	204.4
IR: ν(CO) (cm^{-1}) (pentane)	2025(w), 1927(s), 1919(m), 1883(w)		

a) NMR data in $CDCl_3$ at 25 °C.

The pattern of the ν(CO) bands observed for the complex **32** indicates a tetracarbonyl tungsten arrangement. The ^1H and ^{13}C NMR spectra of complex **32** are similar to the spectra of the complex **15** which were shown in Chapter 3.

The chemical shift of the proton at the 1-position of the cyclohepta-2,4,6-trienyl ring ($\delta(H^{1})$ 3.69, $\delta(H^{1'})$ 4.29) shifted down-field compared with those at the corresponding position in the di(1-cyclohepta-2,4,6-trienyl) amine (**25**) ($\delta(H^{1})$ 3.03). The signal of $H^{1'}$ belonging to the coordinated cyclohepta-2,4,6-trienyl ring is observed at much lower field as compared with H^{1} in the free cyclohepta-2,4,6-trienyl substituent. The signals of the coordinated double bond ($H^{4',5'}$ and $C^{4',5'}$) are shifted upfield ($\delta(H^{4', 5'})$ 5.58, $\delta(C^{4', 5'})$ 123.4) compared with the amine ligand **25** ($\delta(H^{4, 5})$ 6.66, $\delta(C^{4, 5})$ 130.9). In addition, the composition of complex **32** can also be deduced from the EI mass spectrum, which shows the molecular ion peak (m/e 493) and characteristic fragments formed by loss of a C_7H_7 ring and CO ligands.

Chapter 5
Experimental

5.1 General Experimental Conditions

All chemical manipulations, distillations, reactions and subsequent product isolations and purifications were carried out under an atmosphere of prepurified argon (4 Å molecular sieve (Merck) and BTS catalyst (Fluka)) using conventional inert-atmosphere techniques [139]. Products were stored in the dark under inert atmosphere.

The solvents, such as pentane, hexane, toluene, diethyl ether and tetrahydrofuran, were pre-dried over potassium hydroxide and distilled from sodium/potassium alloy. Dichloromethane and acetonitrile were distilled from phosphorus pentoxide (P_4O_{10}). All solvents were distilled and saturated with argon. The deuterated solvents (C_6D_6, $CDCl_3$, CD_2Cl_2) were dried over molecular sieve.

5.2 Irradiation and Column Chromatography

Irradiations were carried out with a high-pressure mercury lamp TQ 718 (Heraeus, Original Hanau, 700 W). The reaction solutions were irradiated in Duran glass Schlenk tubes which were fixed close to the UV lamp and cooled in a water bath (about 15 °C).

Column chromatography was used to separate the product mixtures over silica-gel (Merck, silica-gel 60, grain size 0.06-0.2 mm) which had been pre-dried at about 400 °C under argon for about 5 h (to remove the water) and then stored under argon.

5.3 Physical Measurements (Instrumentation)

5.3.1 Infrared Spectroscopy

The IR spectroscopic measurements were carried out on a Perkin Elmer 983 G.

The typical range for stretching frequencies of the carbonyl group is 2200 cm^{-1} to 1600 cm^{-1}. The following abbreviations for band intensities which are shown in the tables were used.

vs: very strong
s: strong
m: middle
w: weak

vw: very weak
br: broad
sh: shoulder

5.3.2 NMR Spectroscopy

The NMR data in the tables are characterized by the following abbreviations:

δ:	chemical shift
ppm:	parts per million
s:	singlet
d:	doublet
dd:	doublet of doublets
m:	multiplet
t:	triplet
dt:	doublet of triplets

The NMR spectra were measured with a Bruker ARX 250. The samples were prepared in NMR tubes with a diameter of 5 mm under argon. The standard temperature for measuring was 293 K. The chemical shift δ is given in ppm, the chemical shift of the deuterated solvents is

^{1}H (TMS, ext.): $\Xi^{1}H$ = 100.000 MHz; δ = 7.15 ppm for C_6D_6, 7.24 ppm for $CDCl_3$ and 5.32 ppm for CD_2Cl_2.

^{13}C (TMS, ext.): $\Xi^{13}C$ = 25.144 MHz; δ = 128.0 ppm for C_6D_6, 77.0 ppm for $CDCl_3$ and 53.8 ppm for CD_2Cl_2.

5.3.3 Elememtal Analyses

The elemental analyses were performed by Mikroanalytisches Labor Pascher, Remagen-Bandorf.

5.3.4 Mass Spectra

The EI-MS (Electron Ionization-Mass Spectra) were measured on a Finnigan MAT 8500 under electron impact (ionization energy 70 eV). The samples were measured either directly as solids or dissolved in a solvent. FD-MS (Field Desorption-Mass Spectra) were measured using a Varian MAT 311 A. The calculation of the relative mass of the molecular and the fragment ions was carried out by the program Finnigan, List Version 7.0. The following isotopes were used as the basis for

the calculations:

^{1}H, ^{11}B, ^{12}C, ^{14}N, ^{16}O, ^{32}S, ^{35}Cl, ^{52}Cr, ^{81}Br

5.3.5 Crystal Structure Analyses

The crystal structure determinations were carried out in general on both Siemens P4 diffractometer and STOE IPDS (Image Plate Diffraction System) I, respectively, (Mo-K_α-radiation, λ = 71.073 pm, graphite monochromated). The crystals were picked up under argon and mounted in a glass capillary tube. Structure solution and refinement were carried out with the program package SHELXTL-PLUS V.5.1. Measuring temperature for all the crystals was 293 K.

5.4 Starting Materials

The following compounds were obtained commercially and used without further purification:

Acros: bis(trimethylsily)selenide $Se(SiMe_3)_2$, *tert*-butyl isocyanide $(CH_3)_3C$-NC, hexacarbonyl chromium $Cr(CO)_6$, hexacarbonyl molybdenum $Mo(CO)_6$, hexacarbonyl tungsten $W(CO)_6$, decacarbonyl dimanganese $Mn_2(CO)_{10}$;

Fluka: cycloheptatriene C_7H_8, sodium bicarbonate $NaHCO_3$, maleimide $C_4H_3O_2N$, N-phenyl maleimide $C_{10}H_7O_2N$, norbonadiene C_7H_8, mesitylene C_9H_{12}, trimethyl phosphite $P(OMe)_3$, diphenylamine Ph_2NH;

Merck: bromine Br_2, zinc dust Zn, maleic anhydride $C_4H_2O_3$, aniline $PhNH_2$.

The following compounds were prepared according to the quoted literature procedures:

Compound	Lit.	Compound	Lit.
$C_7H_7^+Br^-$	[12]	$C_7H_7^+BF_4^-$	[141]
$Cr(CO)_4(\eta^4\text{-}C_7H_8)$	[99]	$(\eta^6\text{-}C_6H_3Me_3)Mo(CO)_3$	[107]
$Mo(CO)_4(\eta^4\text{-}C_7H_8)$	[99]	$CpMn(CO)_3$	[140]
$Cr(CO)_{6-x}(CH_3CN)_x$	[100]	$Mn(CO)_5Cl$	[110]
$Mo(CO)_{6-x}(CH_3CN)_x$	[100]	$Mn(CO)_5Br$	[110]
$W(CO)_{6-x}(CH_3CN)_x$	[100]	$Fe_3(CO)_{12}$	[142]

5.5 Syntheses

5.5.1 Di(1-cyclohepta-2,4,6-trienyl) chalcogen derivatives, (E = O, S, Se)

Di(1-cyclohepta-2,4,6-trienyl) ether, $O(C_7H_7)_2$ [cf. 8]

A solution of 1.026 g (6 mmol) of tropylium bromide in 10 ml of water was treated with 10 ml of 2N sodium bicarbonate solution. Carbon dioxide was vigorously evolved. The resulting turbid mixture was extracted with four 30-ml portions of pentane, the pentane extract was dried over magnesium sulfate ($MgSO_4$) and the solvent was removed under high vacuum. The residue was distilled at 100-110 °C at 0.5 mmHg to give the product as an almost colorless oil.
Yield: 454 mg (76.4 %).

*Di(1-cyclohepta-2,4,6-trienyl) thioether, $S(C_7H_7)_2$ (**1**) [cf. 12]*

Saturation of a solution of 1.026 g (6 mmol) of tropylium bromide in 50 ml of water with hydrogen sulfide led to the precipitation of an oil which was extracted with ether. The extract was dried over magnesium sulfate ($MgSO_4$) overnight and concentrated. Crystallization on cooling afforded ditropyl thioether (**1**) as light yellow crystals. Two recrystallizations from pentane gave ditropyl thioether as colorless crystals.
Yield: 557 mg (86.8 %), m.p. 34 °C (cf. [12] 37-38 °C, [93] 36 °C).

*Di(1-cyclohepta-2,4,6-trienyl) selenoether, $Se(C_7H_7)_2$ (**2**)*

The suspension of 342 mg (2 mmol) tropylium bromide in 10 ml of dry CH_2Cl_2 was treated with 0.25 ml (1 mmol) of bis(trimethylsilyl)selenide. The mixture was stirred at room temperature and became homogeneous after 30 min. Evaporation of the solvent gave a yellow solid which was dried under high vacuum to remove $BrSiMe_3$. Recrystallization from CH_2Cl_2 afforded yellow crystals.
Yield: 235 mg (90 %), m.p. 62 °C (cf. [84] 64.7-65.2 °C).

5.5.2 Ditropyl

*1,1'-Di(1-cyclohepta-2,4,6-trienyl), $(C_7H_7)_2$ (**3**) [cf. 12]*

A solution of 513 mg (3 mmol) of tropylium bromide in 10 ml of water was shaken vigorously with 200 mg of zinc dust. The mixture became warm and the yellow color of the solution rapidly disappeared. Extraction with four 20-ml portions of pentane, followed by evaporation of the solvent gave a solid residue. Sublimation of the residue at 65-75 °C and 0.5 mmHg afforded a colorless crystalline sublimate.
Yield: 252 mg (92.3 %).

*5.5.3 Diels-Alder Reactions (1:1) with **1** and **3***

*$S(C_7H_7)_2(C_4H_2O_3)$ (**4a**)*

A solution of 214 mg (1 mmol) ditropyl thioether, $S(C_7H_7)_2$ (**1**), and 98 mg (1 mmol) maleic anhydride, $C_4H_2O_3$, in 20 ml of THF was heated under reflux for 2 days. The solvent was removed under high vacuum and the residue was washed with ether repeatedly. Then the ether solution was concentrated and cooled to -28 °C. The adduct **4a** was obtained as light yellow crystals.

Yield: 268 mg (85.9 %), m.p. 115 °C.

FD-MS: 312 [M^+].

*$S(C_7H_7)_2(C_4H_3O_2N)$ (**4b**)*

The adduct **4b** was synthesized by a similar procedure to **4a**. A solution of 214 mg (1 mmol) ditropyl thioether, $S(C_7H_7)_2$ (**1**), and 97 mg (1 mmol) maleimide, $C_4H_3O_2N$, in THF was kept refluxing for 2 days. The solvent was removed in a high vacuum and the residue was washed with ether repeatedly. Then the ether solution was concentrated and cooled to -28 °C. The adduct **4b** was isolated as white crystals.

Yield: 258 mg (83 %), m.p. 177 °C.

EI-MS: *m/e* = 311 (15 %) [M^+], 220 (11 %) [$S(C_7H_7)(C_4H_3O_2N)^+$], 149 (10 %) [$S(C_7H_7)(C_2H_2)^+$], 123 (4 %) [$S(C_7H_7)^+$], 91 (100 %) [$C_7H_7^+$].

*$S(C_7H_7)_2(C_{10}H_7O_2N)$ (**4c**)*

The analogous reaction was carried out with N-phenyl maleimide, $C_{10}H_7O_2N$, as the starting compound. The adduct **4c** was obtained as white crystals.

Yield: 293 mg (75.7 %), m.p. 167 °C.

EI-MS: *m/e* = 387 (10 %) [M^+], 296 (8 %) [$S(C_7H_7)(C_{10}H_7O_2N)^+$], 149 (15 %) [$S(C_7H_7)(C_2H_2)^+$], 117 (55 %) [$(C_7H_7)(C_2H_2)^+$], 91 (100 %) [$C_7H_7^+$].

*$(C_7H_7)_2(C_4H_2O_3)$ (**5a**)*

The 1:1 addition compound **5a** was synthesized by a similar route as **4a**. A solution of 182 mg (1 mmol) ditropyl, $(C_7H_7)_2$ (**3**), and 98 mg (1 mmol) maleic anhydride, $C_4H_2O_3$, in THF was heated to reflux for 2 days. The solvent was then removed in a high vacuum and the residue extracted with ether repeatedly. The ether solution was concentrated and cooled in -28 °C. The adduct **5a** crystallized as white solid.

Yield: 220 mg (78.6 %), m.p. 132 °C.

EI-MS: *m/e* = 280 (9 %) [M^+], 207 (19 %) [$(C_7H_7)(C_7H_6)(C_2H_2)^+$], 181 (13 %) [$(C_7H_7)(C_7H_6)^+$], 91 (100 %) [$C_7H_7^+$].

*$(C_7H_7)_2(C_4H_3O_2N)$ (**5b**)*

The analogous reaction was carried out with maleimide, $C_{10}H_7O_2N$, as the starting

compound. The adduct **5b** was obtained as white crystals.
Yield: 212 mg (76.0 %), m.p. 146 °C.
EI-MS: *m/e* = 279 (9 %) [M^+], 207 (7 %) [$(C_7H_7)(C_7H_6)(C_2H_2)^+$], 181 (30 %) [$(C_7H_7)(C_7H_6)^+$], 91 (100 %) [$C_7H_7^+$].

*$(C_7H_7)_2(C_{10}H_7O_2N)$ (**5c**)*
The analogous reaction with N-phenyl maleimide, $C_{10}H_7O_2N$, as the starting compound gave **5c** as white crystals.
Yield: 256 mg (72.1 %), m.p. 158 °C.
EI-MS: *m/e* = 355 (14 %) [M^+], 264 (9 %) [$(C_7H_7)_2(C_4H_2O_2)^+$], 208 (8 %) [$(C_7H_7)_2(C_2H_2)^+$], 181 (24 %) [$(C_7H_7)(C_7H_6)^+$], 91 (100 %) [$C_7H_7^+$].

*5.5.4 Coordination Compounds Derived from $S(C_7H_7)_2$ (**1**)*

*[Di(1-cyclohepta-2,4,6-trienyl) sulfane] pentacarbonylchromium, $Cr(CO)_5[S(C_7H_7)_2]$ (**6**)*
A tetrahydrofuran (THF) solution (10 ml) containing 214 mg (1 mmol) $S(C_7H_7)_2$ (**1**) was slowly added to an orange solution of $Cr(CO)_{6-x}(CH_3CN)_x$ (x = 1, 2, 3) (~1 mmol) in 50 ml of THF. The reaction mixture was stirred at room temperature overnight. Then the solvent was removed under high vacuum, the residue dissolved in pentane and the solution filtered over filter flocks. The filtrates were concentrated and cooled to -28 °C; the product slowly crystallized as orange crystals.
Yield: 155 mg (38.2 %), m.p. 77 °C under slow decomposition; total decomposition at 83 °C.
FD-MS: 406 [M^+].

*[Benzyl-(1-cyclohepta-2,4,6-trienyl) sulfane] pentacarbonylchromium, $Cr(CO)_5[PhCH_2S(C_7H_7)]$ (**7**)*
Method a):
A solution of 220 mg (1 mmol) $Cr(CO)_6$ in 100 ml of THF was irradiated for 6 hours (with a high pressure mercury arc lamp, 700W), until the ν(CO) absorption of $Cr(CO)_6$ in the IR spectrum had almost disappeared. Then 214 mg (1 mmol) of ditropyl thioether (**1**) was added to the yellow THF solution and the reaction mixture was stirred at room temperature for 2 days. The dark orange solution was concentrated and given on top of a chromatography column filled with silica in pentane (elution with pentane : THF (10:1)). The product was isolated as yellow-green crystals.
Yield: 187 mg (46.1 %), m.p. 65 °C (where decomposition begins).
FD-MS: 406 [M^+].

Method b):
214 mg (1 mmol) of ditropyl thioether (**1**) was added to the solution of 256 mg (1 mmol) $Cr(CO)_4(\eta^4\text{-}C_7H_8)$ in 30 ml of THF. The reaction mixture was stirred at room temperature for 2 days. Then the solvent was removed under high vacuum, the residue dissolved in pentane and the solution filtered over filter flocks. The filtrates were concentrated and cooled to -28 °C. The product crystallized as yellow-green crystals.
Yield: 165 mg (40.6 %).

Method c):
203 mg (0.5 mmol) of complex $Cr(CO)_5[S(C_7H_7)_2]$ (**6**) was dissolved in 20 ml of THF. The solution was stirred at 60 °C for 5 h. Then the dark orange solution was concentrated and separated by chromatography column (elution with pentane : THF = 10:1). The product was again isolated as yellow-green crystals.
Yield: 115 mg (56.7 %).

[Di(1-cyclohepta-2,4,6-trienyl) sulfane] pentacarbonylmolybdenum,
*$Mo(CO)_5[S(C_7H_7)_2]$ (**9**)*
A THF solution (10 ml) containing 214 mg (1mmol) $S(C_7H_7)_2$ (**1**) was slowly added to an orange solution of $Mo(CO)_{6-x}(CH_3CN)_x$ (x = 1, 2, 3) (obtained from 1 mmol of $Mo(CO)_6$) in 50 ml of THF. The reaction mixture was stirred at room temperature overnight. Then the solvent was removed under vacuum, the residue dissolved in pentane and the solution filtered over filter flocks. The filtrates were concentrated and cooled to -28 °C to give dark-yellow crystals.
Yield: 175 mg (38.9 %), m.p. 70 °C (beginning decomposition).

[Di(1-cyclohepta-2,4,6-trienyl) sulfane] tetracarbonylmolybdenum,
*$Mo(CO)_4[(\eta^2\text{-}C_7H_7)S(C_7H_7)]$ (**10**)*
Method a):
A solution of 264 mg (1 mmol) $Mo(CO)_6$ in 100 ml of THF was irradiated 3-5 hours (with a high pressure mercury arc lamp, 700W), until the ν(CO) absorption band of $Mo(CO)_6$ had nearly disappeared. Then 214 mg (1 mmol) of ditropyl thioether (**1**) was added to the yellow THF solution, and the reaction mixture was stirred at room temperature for 20 h. The solvent was removed under high vacuum, the residue dissolved in ether and the ether solution filtered over filter flocks. The filtrates were concentrated and cooled to -28 °C in the refrigerator; the product slowly crystallized as yellow crystals.
Yield: 146 mg (34.6 %), m.p. 80 °C (beginning decomposition); total decomposition at 95 °C.
FD-MS: 424 $[M^+]$.

Method b):
214 mg (1 mmol) of ditropyl thioether (**1**) was added to the solution of 300 mg (1 mmol) $Mo(CO)_4(\eta^4\text{-}C_7H_8)$ in 30 ml of THF. The reaction mixture was stirred at room temperature for 2 days. Then the solvent was removed under high vacuum, the residue dissolved in pentane and the solution filtered over filter flocks. The filtrates were concentrated and cooled to -28 °C. The product was obtained as yellow crystals.
Yield: 175 mg (41.3 %).

Method c):
During the preparation of complex $Mo(CO)_5[S(C_7H_7)_2]$ (**9**), $Mo(CO)_4[(\eta^2\text{-}C_7H_7)S(C_7H_7)]$ (**10**) was also obtained in very low yield.
Yield: 40 mg (9.4 %).

*[Ditropyl] tricarbonylmolybdenum, $Mo(CO)_3[(C_7H_7)_2]$ (**12**)*
A mixture of 264 mg (1 mmol) $Mo(CO)_6$ and 214 mg (1 mmol) $S(C_7H_7)_2$ (**1**) in 50 ml of THF was heated under reflux for 1 day. The solvent was removed under high vacuum and the residue dissolved in ether. The ether solution was reduced to 2 ml and chromatographed over silica. Elution with pentane : THF (10:1) gave **12a** and **12b**, which were isolated as orange crystals.
Yield: 85 mg (23.4 %) (**12a**) and 37 mg (10.2 %) (**12b**), m.p. 131 °C.
FD-MS: 364 $[M^+]$.

*[Di(1-cyclohepta-2,4,6-trienyl) sulfane] pentacarbonyltungsten, $W(CO)_5[S(C_7H_7)_2]$ (**13**)*
Method a):
A solution of 352 mg (1 mmol) $W(CO)_6$ in 100 ml of THF was irradiated 7 hours (with a high pressure mercury arc lamp, 700W), until the ν(CO) absorption band of $W(CO)_6$ had almost disappeared. Then 214 mg (1 mmol) ditropyl thioether (**1**) was added to the yellow THF solution and the reaction mixture was stirred at room temperature for 1 day. The orange-brown solution was concentrated and separated by column chromatography (pentane : THF = 10:1). The product was obtained as light-yellow crystals.
Yield: 310 mg (57.6 %), m.p. 55 °C (beginning decomposition).

Method b):
Complex **13** could be isolated by column chromatography during the preparation of the complex **15**. Complex **13** was given as light-yellow crystals in low yield.
Yield: 78 mg (14.5 %).

[Benzyl-(1-cyclohepta-2,4,6-trienyl) sulfane] pentacarbonyltungsten,
$W(CO)_5[PhCH_2S(C_7H_7)]$ ***(14)***

Method a):

The THF solution of $W(CO)_5$(thf) and ditropyl thioether (**1**) (1:1) was stirred at 40 °C for 1 day. Then the dark brown solution was concentrated and worked up by column chromatography. Elution with pentane : THF (10:1) gave a yellow solution from which yellow crystals of **14** could be obtained.

Yield: 268 mg (49.8 %), m.p. 55 °C (dec.).

Method b):

269 mg (0.5 mmol) of complex $W(CO)_5[S(C_7H_7)_2]$ (**13**) was dissolved in 20 ml of THF. The solution was stirred at 50 °C for 5 h. Then the dark orange solution was concentrated and seperated by chromatography column (elution with pentane : THF = 10:1). The product was isolated as yellow crystals.

Yield: 142 mg (52.8 %).

[Di(1-cyclohepta-2,4,6-trienyl) sulfane] tetracarbonyltungsten,
$W(CO)_4[(\eta^2\text{-}C_7H_7)S(C_7H_7)]$ ***(15)***

A tetrahydrofuran (THF) solution (10 ml) containing 214 mg (1mmol) $S(C_7H_7)_2$ (**1**) was slowly added to an orange-red solution of $W(CO)_{6-x}(CH_3CN)_x$ (x = 1, 2, 3) in 50 ml of THF. The reaction mixture was stirred at room temperature for 1 day. Then the dark brown solution was concentrated and the mixture was separated by column chromatography. Elution with pentane : THF (10:1) produced a solution from which yellow-orange crystals could be obtained.

Yield: 215 mg (42.2 %), m.p. 105 °C (beginning decomposition); total decomposition at 112 °C.

FD-MS: 510 [M^+].

Bis[(1-cyclohepta-2,4,6-trienyl) thiolato]-octacarbonyldimanganese,
$\{Mn(CO)_4[S(C_7H_7)]\}_2$ ***(17)***

Method a):

A solution of 195 mg (0.5 mmol) $Mn_2(CO)_{10}$ and 214 mg (1 mmol) $S(C_7H_7)_2$ (**1**) in 100 ml of THF was irradiated for 30 mins (with a high pressure mercury arc lamp, 700W). Then the solvent was removed under vacuum, the residue dissolved in pentane and the solution filtered over filter flocks. The filtrate was concentrated and cooled to -28 °C, the product was obtained as yellow crystals.

Yield: 174 mg (60.0 %), m.p. 88 °C (beginning decomposition).

FD-MS: 580 [M^+].

Method b):
The dichloromethane solution of $Mn(CO)_5X$ (X = Cl, Br) and ditropyl thioether (**1**) (1:1) was stirred at room temperature overnight. Then the dark brown solution was concentrated and worked up by column chromatography. Elution with pentane : THF (10:1) gave a yellow solution from which yellow crystals of **17** could be isolated.
Yield: 146 mg (50.3 %).

*Bis[(1-cyclohepta-2,4,6-trienyl) thiolato]-di(tert-butylisocyanide) hexacarbonyldimanganese, {Mn(CO)$_3$[^{t}BuNC][S(C$_7$H$_7$)]}$_2$ (**18**)*
115 µl (1 mmol) of *tert*-butyl isocyanide was added to a solution of 290 mg (0.5 mmol) $\{Mn(CO)_4[S(C_7H_7)]\}_2$ in 20 ml of THF. The reaction mixture was stirred at 35 °C overnight, whereby the color of the solution changed from orange to yellow. The solvent was removed under vacuum, and the residue was dissolved in CH_2Cl_2. Concentration and cooling to -28 °C gave yellow crystals.
Yield: 278 mg (80.6 %), m.p. 80 °C (beginning decomposition).

*Bis[(1-cyclohepta-2,4,6-trienyl) thiolato]-di(trimethylphosphite) hexacarbonyldimanganese, {Mn(CO)$_3$[P(OMe)$_3$][S(C$_7$H$_7$)]}$_2$ (**19**)*
120 µl (1 mmol) of $P(OMe)_3$ was added to a solution of 290 mg (0.5 mmol) $\{Mn(CO)_4[S(C_7H_7)]\}_2$ in 20 ml of THF. The orange reaction mixture was stirred at room temperature overnight; the color of the solution slowly changed to yellow. The solvent was removed under vacuum and the residue dissolved in CH_2Cl_2. It was concentrated and cooled to -28 °C; the product was isolated as yellow crystals.
Yield: 320 mg (82.9 %), m.p. 75 °C (beginning decomposition).

*Reaction of S(C$_7$H$_7$)$_2$ (**1**) with CpMn(CO)$_3$:*
*Formation of [CpMn(CO)$_2$]$_2$(µ-S) (**21**) and [CpMn(CO)$_2$]$_2$(µ-SO) (**22**) [cf. 111]*
A solution of 204 mg (1 mmol) $CpMn(CO)_3$ in 100 ml of THF was irradiated for 2 hours (with a high pressure mercury arc lamp, 700W). Then 214 mg (1 mmol) of ditropyl thioether (**1**) was added to the red THF solution, and the reaction mixture stirred at room temperature for 1 h. Then the dark brown solution was concentrated and worked up by column chromatography. Elution using pentane : THF (10:1) gave the known [111] dinuclear complexes **21** (green) and **22** (violet).
Yield: 35 mg (18.2 %) (**21**), 18 mg (9.0 %) (**22**).

*Reaction of S(C$_7$H$_7$)$_2$ (**1**) with Fe$_3$(CO)$_{12}$:*
*Attempts to prepare Fe(CO)$_4$[S(C$_7$H$_7$)$_2$] (**23**)*
A solution of 168 mg (0.33 mmol) $Fe_3(CO)_{12}$ in 100 ml of THF was irradiated for 2 hours (with a high pressure mercury arc lamp, 700W), until the ν(CO) absorptions of $Fe_3(CO)_{12}$ had disappeared. Then 214 mg (1 mmol) ditropyl thioether (**1**) was added

to the red THF solution and the reaction mixture stirred at room temperature for 1 day. The solvent was removed under high vacuum, the residue dissolved in pentane and filtered over filter flocks. The filtrates were concentrated and cooled at -28 °C, the product slowly crystallized as dark-red crystals.
Yield: 156 mg (40.8 %), m.p. 83 °C (beginning decomposition).

5.5.5 Reactions with (1-cyclohepta-2,4,6-trienyl) amines

*Tri(1-cyclohepta-2,4,6-trienyl) amine, $N(C_7H_7)_3$ (**24**) [cf. 12]*
A suspension of 1.026 g (6 mmol) of tropylium bromide in 100 ml of dry ether was cooled to 0 °C in an ice bath. The mixture was saturated with ammonia and stirred for 40 min while ammonia was continuously passed through the mixture. The reaction mixture was filtered from ammonium bromide, concentrated and cooled to give light yellow crystals. Two recrystallizations from ether afforded **24** as colorless, transparent crystals.
Yield: 370 mg (64.5 %), m.p. 122 °C (cf. [12,132] 124-125 °C).

*Di(1-cyclohepta-2,4,6-trienyl) amine, $NH(C_7H_7)_2$ (**25**) [cf. 12]*
A solution of 1.026 g (6 mmol) of tropylium bromide in 5 ml of water was added dropwise with stirring to 60 ml of cool, concentrated aqueous ammonia. An oil was isolated by extraction with pentane followed by concentration. Two recrystallizations from pentane afforded **25** as colorless crystals.
Yield: 300 mg (50.8 %), m.p. 30 °C (cf. [12,132] 28-30 °C).

*Di(1-cyclohepta-2,4,6-trienyl)phenylamine, $N(Ph)(C_7H_7)_2$ (**28**)*
Aniline, $PhNH_2$, (93 mg, 1 mmol) was added to a solution of 342 mg (2 mmol) of tropylium bromide in 20 ml of ethanol. The solution was stirred at room temperature for 2 h. Evaporation of ethanol left a yellow-brown solid. $PhN(C_7H_7)_2$ **(28)** was crystallized from ethanol/pentane and dried under high vacuum.
Yield: 210 mg (76.9 %), m.p. 150 °C (dec.).
EI-MS: *m/e* = 273 (16 %) [M^+], 183 (100 %) [$N(H)(Ph)(C_7H_7)^+$], 182 (33 %) [$(C_7H_7)_2^+$].

*(1-Cyclohepta-2,4,6-trienyl)diphenylamine, $N(Ph)_2(C_7H_7)$ (**29**)*
A solution of Ph_2NH (169 mg, 1 mmol) in 5 ml of ethanol was added dropwise to a solution of 171 mg (1 mmol) of tropylium bromide in 10 ml of ethanol. The mixture was stirred at room temperature for 2 h. $N(Ph)_2(C_7H_7)$ (**29**) was crystallized from ethanol as light-blue solid, which was dried under high vacuum.
Yield: 215 mg (83.0 %), m.p. 134 °C (dec.).
EI-MS: *m/e* = 259 (100 %) [M^+], 169 (80 %) [Ph_2NH^+], 91 (12 %) [$C_6H_5N^+$], 77 (21

%) [$C_6H_5^+$].

*5.5.6 Diels-Alder Reactions with **24** and **25***

*$N(C_7H_7)_3(C_4H_3O_2N)$ **(26b)***

A THF solution of 287 mg (1 mmol) tri(1-cyclohepta-2,4,6-trienyl) amine, $N(C_7H_7)_3$ (**24**), and 291 mg (3 mmol) maleimide, $C_4H_3O_2N$, was heated under reflux for 2 days. The solvent was removed under high vacuum, and the residue was washed with pentane repeatedly to remove unreacted $N(C_7H_7)_3$ (**24**). Crystallization from ether at -28 °C afforded a light yellow solid (**26b**).

Yield: 258 mg (67.2 %), m.p. 107 °C.

EI-MS: *m/e* = 384 (20 %) [M^+], 293 (26 %) [$N(C_7H_7)_2(C_4H_3O_2N)^+$], 117 (32 %) [$(C_7H_7)(C_2H_2)^+$], 91 (100 %) [$C_7H_7^+$].

*$N(C_7H_7)_3(C_{10}H_7O_2N)_2$ **(26c)***

In an analogous manner, the reaction of **24** with N-phenyl maleimide, $C_{10}H_7O_2N$, as the starting compound gave **26c** as a white-yellow solid.

Yield: 357 mg (56.4 %), m.p. 115 °C.

EI-MS: *m/e* = 633 (7 %) [M^+], 460 (11 %) [$N(C_7H_7)_3(C_{10}H_7O_2N)^+$], 370 (41 %) [$HN(C_7H_7)_2(C_{10}H_7O_2N)^+$], 173 (42 %) [$C_{10}H_7O_2N^+$], 117 (29 %) [$(C_7H_7)(C_2H_2)^+$], 91 (100 %) [$C_7H_7^+$].

*$NH(C_7H_7)_2(C_4H_3O_2N)$ **(27b)***

A THF solution containing 197 mg (1 mmol) di(1-cyclohepta-2,4,6-trienyl) amine, $NH(C_7H_7)_2$ (**25**), and 194 mg (2 mmol) maleimide, $C_4H_3O_2N$, was heated to reflux for 2 days. The solvent was removed under high vacuum and the residue washed with pentane to remove unreacted $NH(C_7H_7)_2$ (**25**). Crystallization from ether at -28 °C afforded a yellow solid (**27b**).

Yield: 206 mg (70.1 %), m.p. 122 °C.

*$NH(C_7H_7)_2(C_{10}H_7O_2N)$ **(27c)***

The analogous reaction of **25** with N-phenyl maleimide, $C_{10}H_7O_2N$, as the starting compound led to the yellow solid **27c**.

Yield: 234 mg (63.2 %), m.p. 135 °C.

EI-MS: *m/e* = 370 (16 %) [M^+], 279 (21 %) [$NH(C_7H_7)(C_{10}H_7O_2N)^+$], 173 (68 %) [$C_{10}H_7O_2N^+$], 117 (58 %) [$(C_7H_7)(C_2H_2)^+$], 91 (100 %) [$C_7H_7^+$].

5.5.7 Reaction of (1-Cyclohepta-2,4,6-trienyl) amines with $[C_7H_7]BF_4$: N-tropylidene-(1-cyclohepta-2,4,6-trienyl)immonium tetrafluoroborates

*$[(C_7H_6)NH(C_7H_7)]^+BF_4^-$ (**30**)*

A solution of 287 mg (1 mmol) of $N(C_7H_7)_3$ (**24**) in 5 ml CH_2Cl_2 was added dropwise to the suspension of $[C_7H_7]BF_4$ (178 mg, 1 mmol) in 10 ml of CH_2Cl_2. The mixture was stirred at room temperature and became homogeneous after 30 min. Evaporation of the solvent gave an orange solid which was washed repeatedly with ether. Recrystallization from CH_2Cl_2 afforded orange crystals of $[(C_7H_6)NH(C_7H_7)]^+BF_4^-$ (**30**).

Yield: 123 mg (43.5 %), m.p. 95 °C (dec.).

The analogous reaction was carried out with $NH(C_7H_7)_2$ (**25**) as the starting compound. The product $[(C_7H_6)NH(C_7H_7)]^+BF_4^-$ (**30**) was obtained in slightly higher yield (155 mg, 54.8 %) than from **24**.

Anal. Calcd for $[(C_7H_6)NH(C_7H_7)]^+BF_4^-$: C 59.36 %, H 4.95 %, N 4.95 %, B 3.89 %, F 26.85 %. Found: C 58.42 %, H 4.90 %, N 4.98 %, B 3.96 %, F 26.1 %.

*$[(C_7H_6)N(Ph)(C_7H_7)]^+BF_4^-$ (**31**)*

In analogy to the preparation of **30**, a solution of 273 mg (1 mmol) of $N(Ph)(C_7H_7)_2$ (**28**) in 5 ml CH_2Cl_2 was added dropwise to a suspension of $[C_7H_7]BF_4$ (178 mg, 1 mmol) in 10 ml of CH_2Cl_2. The mixture was stirred for 30 min under ambient temperature and slowly became homogeneous. Evaporation of the solvent gave a dark-red solid which was washed repeatedly with ether and crystallized from CH_2Cl_2. Dark-red crystals of $[(C_7H_6)N(Ph)(C_7H_7)]^+BF_4^-$ (**31**) were obtained.

Yield: 210 mg (58.5 %), m.p. 113 °C.

*5.5.8 Complex Formation of **25***

*[Di(1-cyclohepta-2,4,6-trienyl) amine] tetracarbonyltungsten, $W(CO)_4[(\eta^2\text{-}C_7H_7)NH(C_7H_7)]$ (**32**)*

A THF solution (10 ml) containing 197 mg (1 mmol) $NH(C_7H_7)_2$ (**25**) was slowly added to an orange-red solution of $W(CO)_{6-x}(CH_3CN)_x$ (x = 1, 2, 3) in 50 ml of THF. The reaction mixture was stirred at room temperature for 1 day. Then the solvent was evaporated and the residue was dissolved in ether. The ether solution was concentrated and cooled to -28 °C to give **32** as yellow crystals.

Yield: 275 mg (55.8 %), m.p. 77 °C (beginning decomposition).

EI-MS: *m/e* = 493 (10 %) $[M^+]$, 374 (16 %) $[WN(H)(C_7H_7)(CO)_3^+]$, 318 (25 %) $[WN(H)(C_7H_7)(CO)^+]$, 290 (35 %) $[WN(H)(C_7H_7)^+]$, 91 (100 %) $[C_7H_7^+]$.

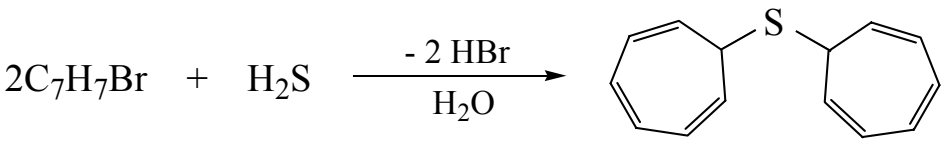
Chapter 6

Summary

This thesis describes the synthesis, characterization and coordination chemistry of di(1-cyclohepta-2,4,6-trienyl) thioether, $S(C_7H_7)_2$ (**1**), tri(1-cyclohepta-2,4,6-trienyl) amine, $N(C_7H_7)_3$ (**24**), and di(1-cyclohepta-2,4,6-trienyl) amine, $NH(C_7H_7)_2$ (**25**). As a potential polydentate ligand system, $S(C_7H_7)_2$ (**1**) has a versatile coordination chemistry.

6.1 Investigations with Di(1-cyclohepta-2,4,6-trienyl) thioether, $S(C_7H_7)_2$ (1)

The reaction of tropylium bromide, C_7H_7Br, with the gas hydrogen sulfide (H_2S) leads to the sulfane **1**.



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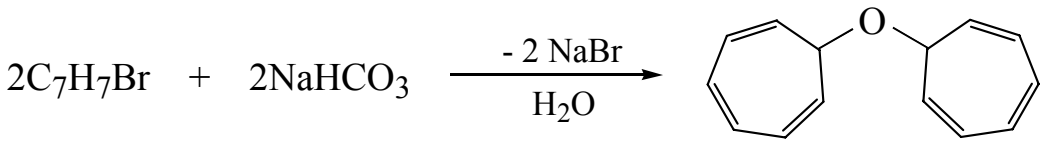
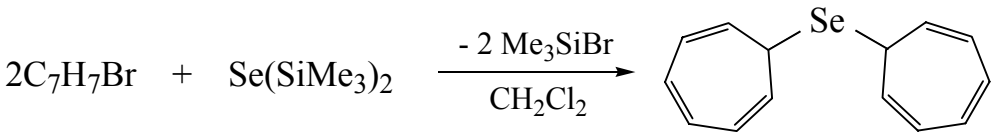
In a similar manner, treatment of an aqueous solution of tropylium bromide with sodium bicarbonate produces di(1-cyclohepta-2,4,6-trienyl) ether.



According to the literature, di(1-cyclohepta-2,4,6-trienyl) selenoether, $(C_7H_7)_2Se$ (**2**), was prepared from tropylium bromide and hydrogen selenide (H_2Se) gas. An attractive alternative is the use of an in-situ source of H_2Se, *i.e.* bis(trimethylsilyl)selenide, $Se(SiMe_3)_2$, in analogy to the preparation of tri(1-cyclohepta-2,4,6-trienyl) phosphane from $P(SiMe_3)_3$. The selane **2** was obtained in high yield.



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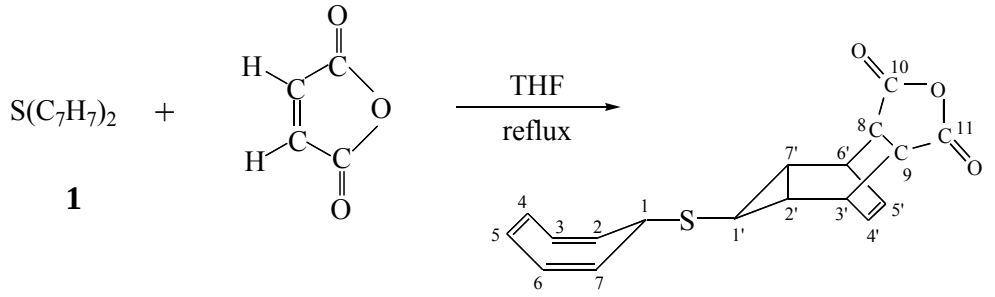
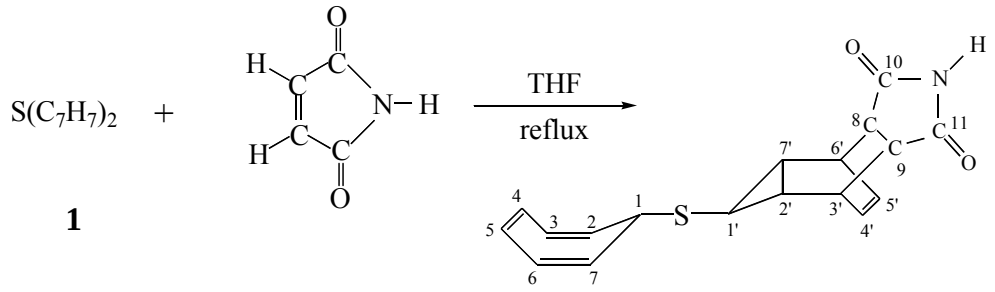
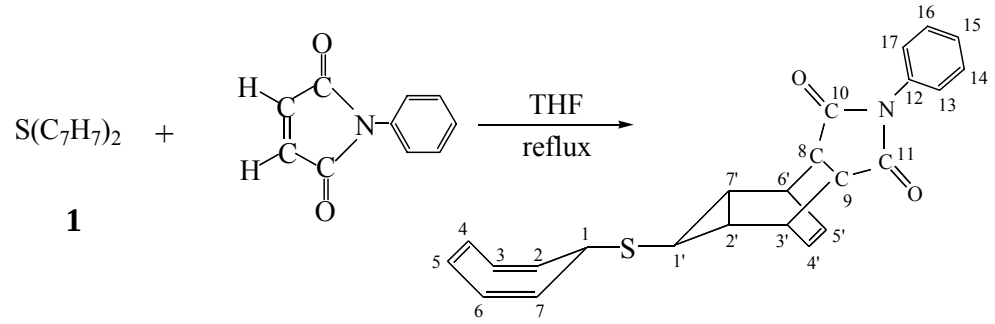
Di(1-cyclohepta-2,4,6-trienyl) thioether, $S(C_7H_7)_2$ (**1**), can undergo Diels-Alder reactions with maleic anhydride, maleimide and N-phenyl maleimide to give **4a**, **4b** and **4c**, respectively. In these three compounds, one cyclohepta-2,4,6-trienyl ring has remained intact, whereas the other seven-membered ring is involved in the Diels-Alder reaction.



1 **4a**



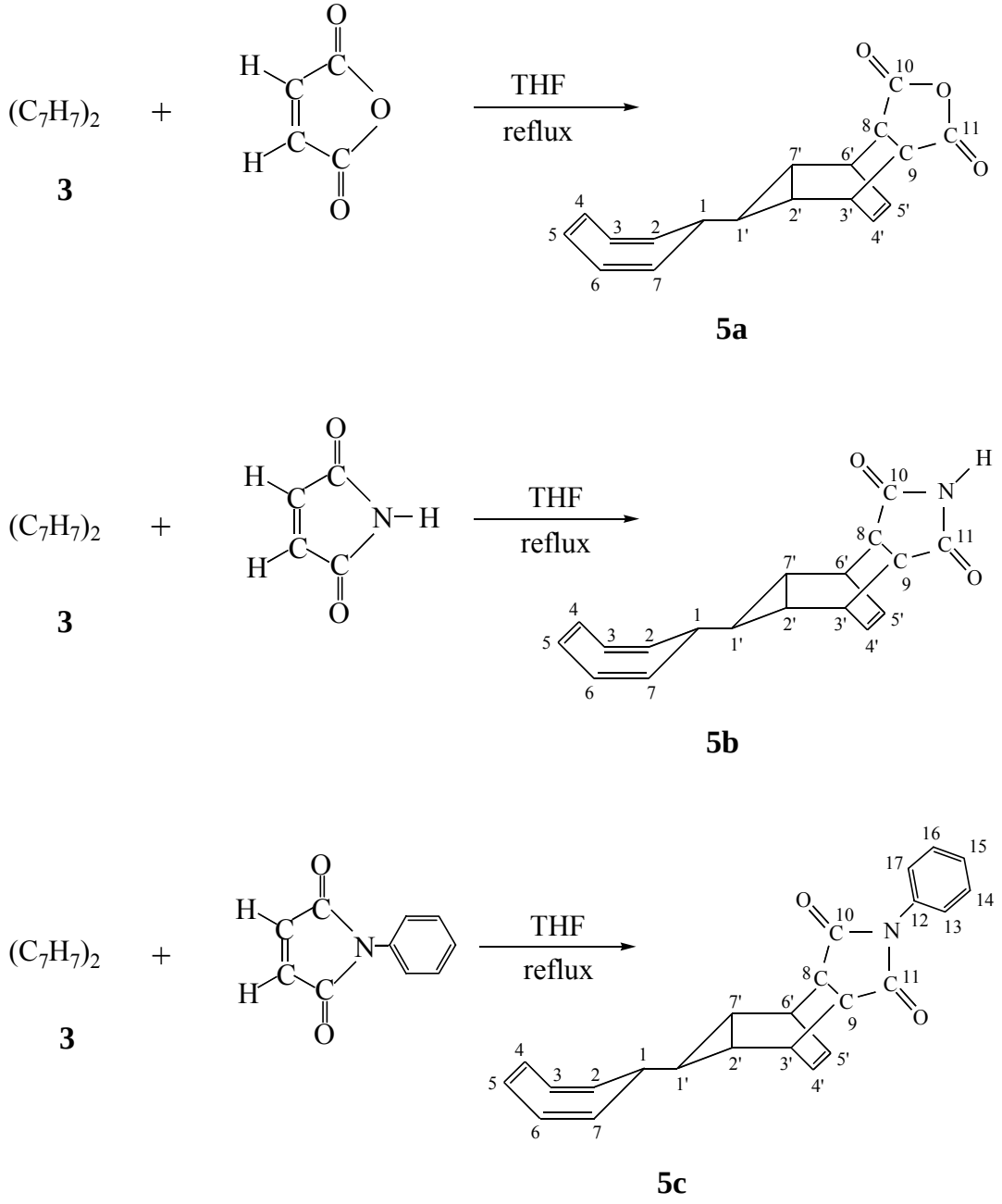
1 **4b**



1 **4c**

Synthesis of the Diels-Alder adducts **4a**, **4b** and **4c**

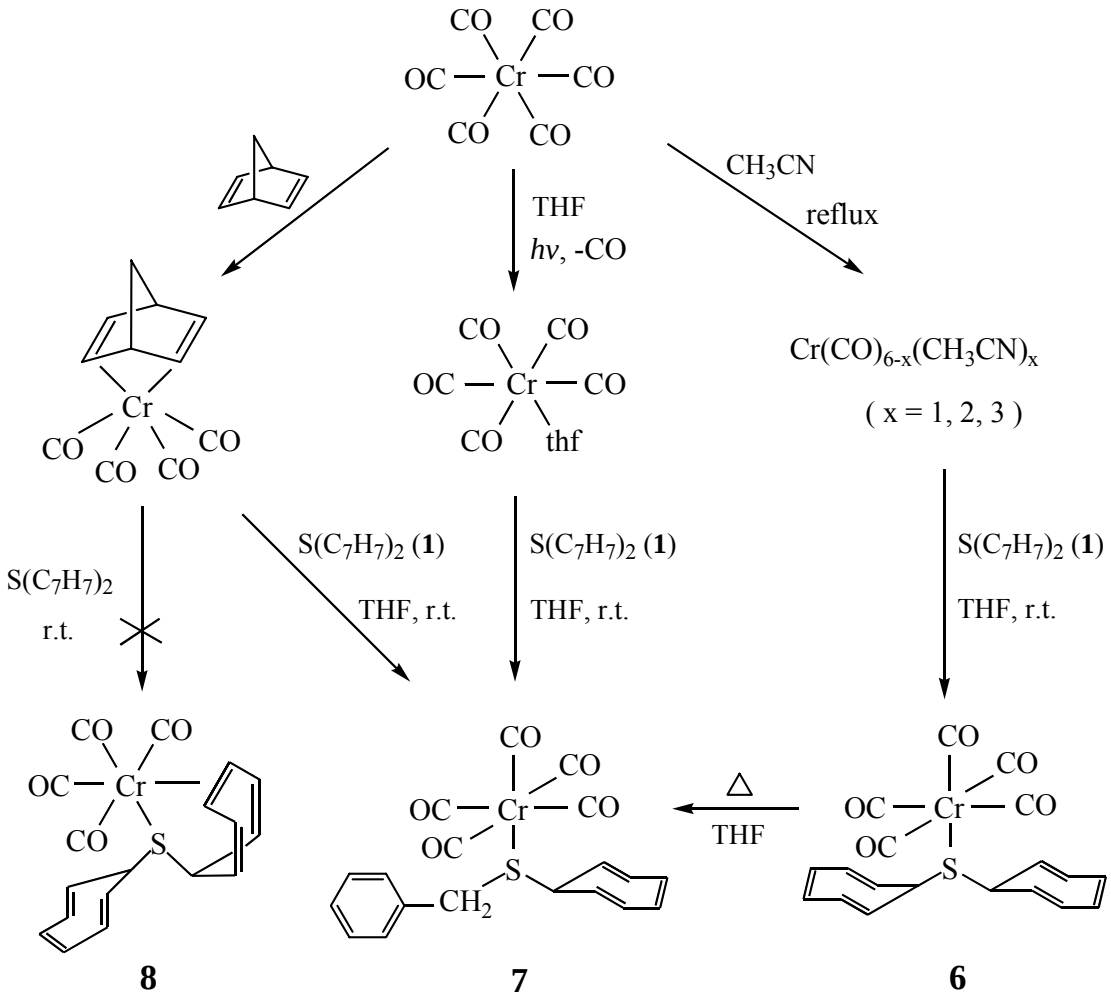
In addition, Diels-Alder reactions of ditropyl, $(C_7H_7)_2$ (**3**), with maleic anhydride, maleimide and N-phenyl maleimide were carried out. The structures of the products **5a**, **5b** and **5c** are similar to the structures of the adducts **4a**, **4b** and **4c**.



Synthesis of the Diels-Alder adducts **5a**, **5b** and **5c**

The advantage of the potential ligand $S(C_7H_7)_2$ (**1**) in comparison to other simple sulfanes is that it can act as a chelate ligand, using one of the non-planar seven-membered rings. In general, the central double bond of one of the seven-membered rings can be coordinated to the metal. The disadvantage of the sulfane **1** is its sensitivity towards oxidation and its low thermal stability.

Towards the complex fragments $[M(CO)_{6-x}]$ (M = Cr, Mo, W; x = 1, 2), the potential ligand $S(C_7H_7)_2$ (**1**) can behave as a two- or four-electron donor. Depending on the steric conditions, the sulfane **1** may also rearrange.

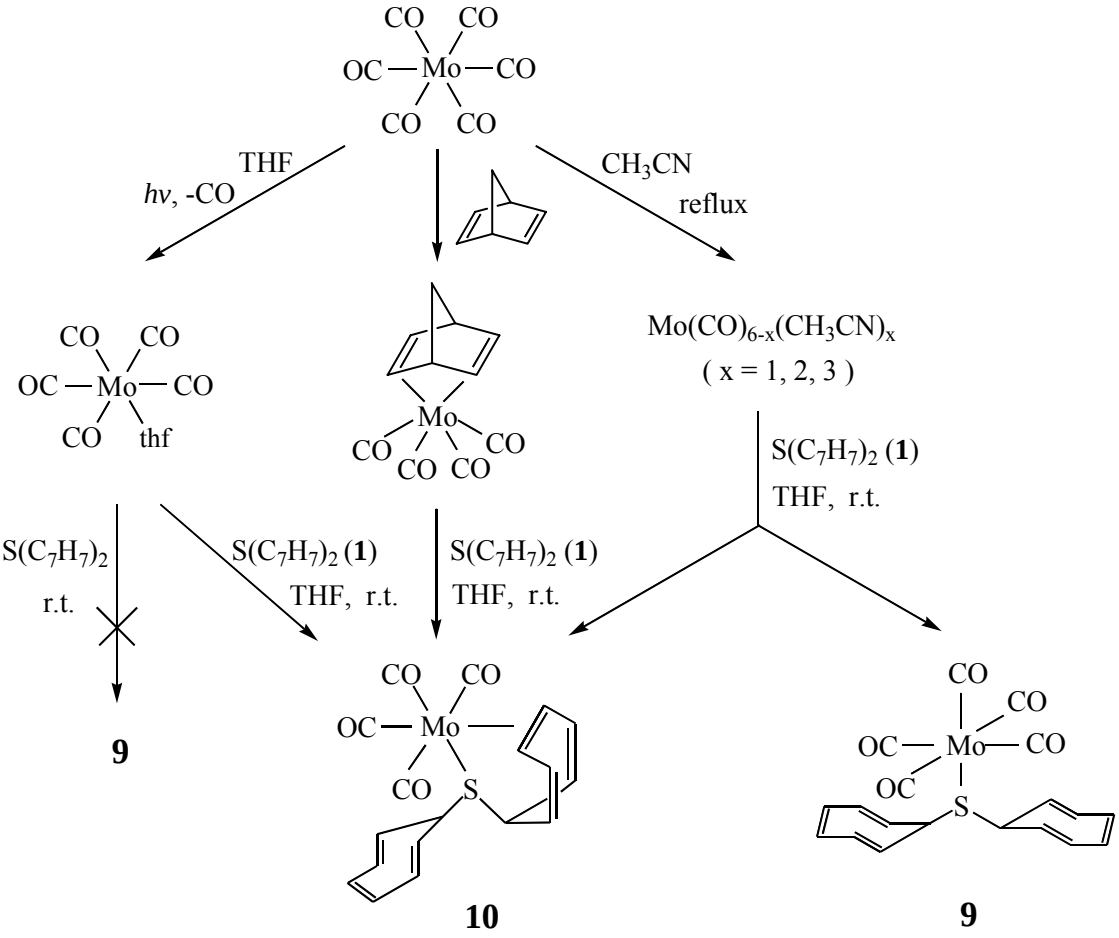


Synthesis of the complexes $Cr(CO)_5[S(C_7H_7)_2]$ (**6**) and $Cr(CO)_5[PhCH_2S(C_7H_7)]$ (**7**)

The reactions of either $Cr(CO)_5(thf)$ or $Cr(CO)_4(\eta^4\text{-}C_7H_8)$ with one equivalent of **1** lead to the monosubstituted derivative $Cr(CO)_5[PhCH_2S(C_7H_7)]$ (**7**), in which one seven-membered ring has remained unchanged and the other seven-membered ring has been transformed to a benzyl group. From a mixture of **1** and chromium(carbonyl)(acetonitrile) complexes, $Cr(CO)_{6-x}(CH_3CN)_x$ (x = 1, 2, 3), complex $Cr(CO)_5[S(C_7H_7)_2]$ (**6**) could be obtained, in which both cycloheptatrienyl ring substituents are freely pending at the sulfur atom.

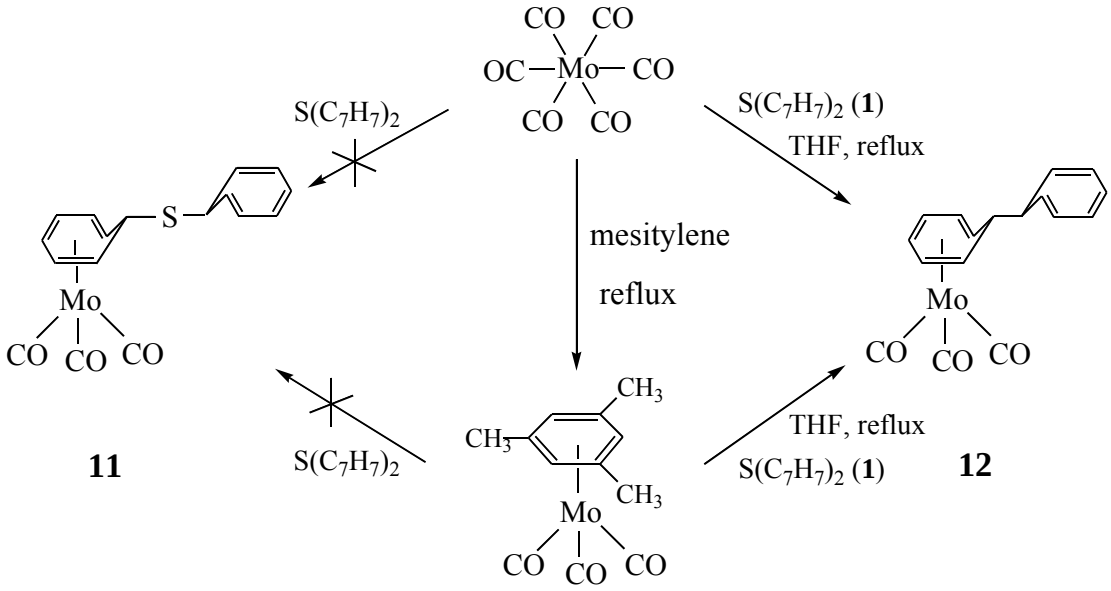
Using the same method as for the chromium complexes, tetracarbonyl molybdenum $Mo(CO)_4[(\eta^2\text{-}C_7H_7)S(C_7H_7)]$ (**10**) was obtained from the reaction of either $Mo(CO)_5(thf)$ or $Mo(CO)_4(\eta^4\text{-}C_7H_8)$ with the potential ligand **1**. In complex **10**

the ligand $S(C_7H_7)_2$ is coordinated to the metal both through a lone pair of electrons at the sulfur atom and the central C=C double bond of a cyclohepta-2,4,6-trienyl substituent. $Mo(CO)_5[S(C_7H_7)_2]$ (**9**) could be obtained from $Mo(CO)_{6-x}(CH_3CN)_x$ (x = 1, 2, 3); in analogy to **6**, the sulfane ligand in **9** is coordinated to molybdenum exclusively through a lone pair of electrons at the sulfur atom.



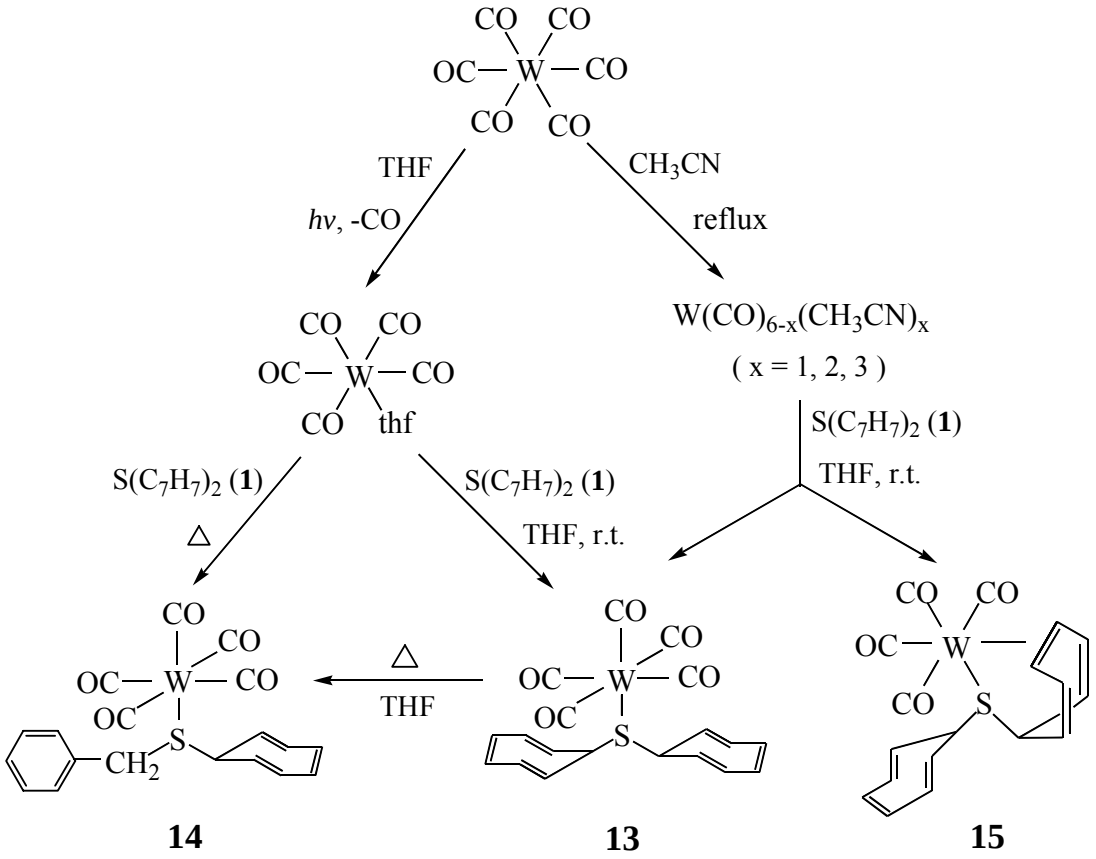
Synthesis of the complexes $Mo(CO)_5[S(C_7H_7)_2]$ (**9**)
and $Mo(CO)_4[(\eta^2\text{-}C_7H_7)S(C_7H_7)]$ (**10**)

When hexacarbonyl molybdenum was reacted with the sulfane **1**, the ligand decomposed and the ditropyl complex $Mo(CO)_3[(\eta^6\text{-}C_7H_7)(C_7H_7)]$ (**12**) was obtained. This indicates the instability of the sulfane **1** in its reactions with metal complexes.



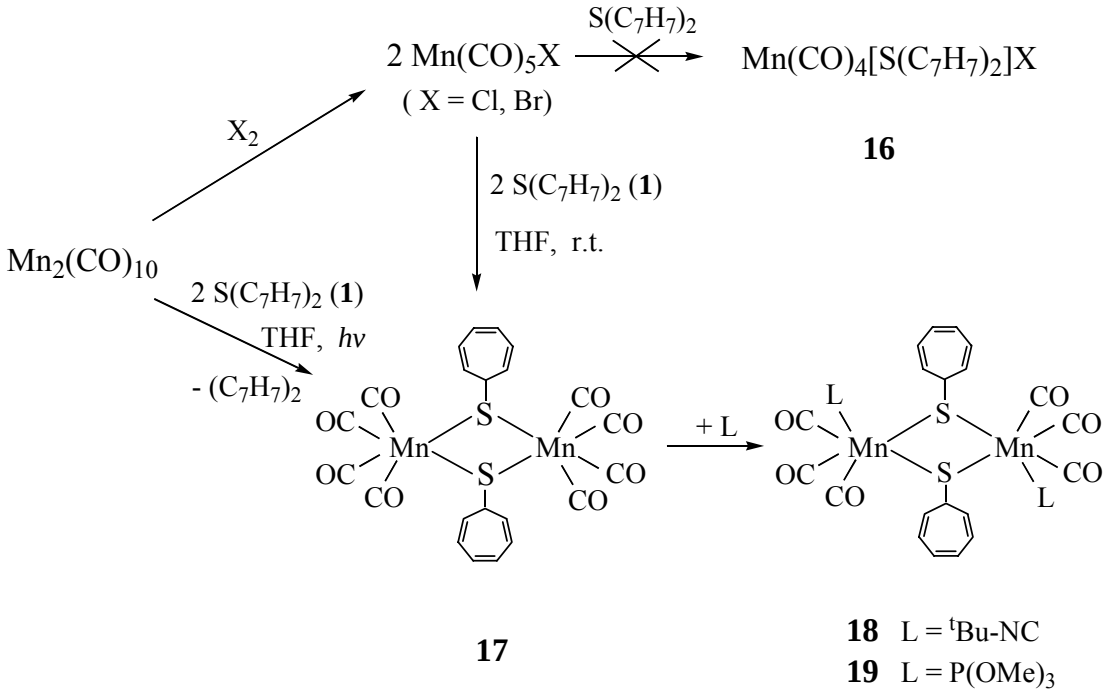
Synthesis of the complex $Mo(CO)_3[(\eta^6\text{-}C_7H_7)(C_7H_7)]$ (**12**)

From the intermediate $W(CO)_5(thf)$, the pentacarbonyltungsten complex $W(CO)_5[S(C_7H_7)_2]$ (**13**) was obtained, which could be converted to the benzyl complex $W(CO)_5[PhCH_2S(C_7H_7)]$ (**14**) when heated in THF solution. Complex **14** has the same structure as the analogous chromium complex **7**, *i.e.* one cyclohepta-2,4,6-trienyl substituent has rearranged to a benzyl group, and the other seven-membered ring remains unchanged. In the reaction with the mixture of tungsten(carbonyl)(acetonitrile) complexes, $W(CO)_{6-x}(CH_3CN)_x$ (x = 1, 2, 3), the compounds $W(CO)_4[(\eta^2\text{-}C_7H_7)S(C_7H_7)]$ (**15**) and $W(CO)_5[S(C_7H_7)_2]$ (**13**) were obtained; complex **15** was the main product. In **15** the olefinic sulfane $S(C_7H_7)_2$ plays the part of a 4-electron ligand as in **10**, bearing one η^2-coordinated and one free cyclohepta-2,4,6-trienyl substituent at the sulfur atom.



Synthesis of the complexes $W(CO)_5[S(C_7H_7)_2]$ (**13**), $W(CO)_5[PhCH_2S(C_7H_7)]$ (**14**) and $W(CO)_4[(\eta^2\text{-}C_7H_7)S(C_7H_7)]$ (**15**)

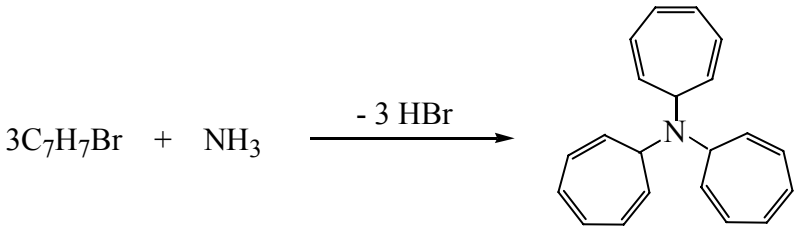
When decacarbonyl dimanganese was reacted with di(1-cyclohepta-2,4,6-trienyl) thioether (**1**) in THF solution under irradiation, the dimeric complex $Mn_2(CO)_8[S(C_7H_7)]_2$ (**17**) was obtained. In this complex the sulfane **1** had lost one ring, and ditropyl had been formed. In addition, complex **17** can also be prepared from precursors such as pentacarbonyl manganese halides, $Mn(CO)_5X$ (X = Cl, Br). It is possible to replace two carbonyl ligands in complex **17** by stronger σ-donor-π-acceptor ligands such as *tert*-butyl isocyanide and trimethyl phosphite (^{t}BuNC and $P(OMe)_3$), respectively, and to synthesize the complexes $Mn_2(CO)_6[^t BuNC]_2[S(C_7H_7)]_2$ (**18**) and $Mn_2(CO)_6[P(OMe)_3]_2[S(C_7H_7)]_2$ (**19**).



Synthesis of the complexes $Mn_2(CO)_8[S(C_7H_7)]_2$ (**17**), $Mn_2(CO)_6[^tBuNC]_2[S(C_7H_7)]_2$ (**18**) and $Mn_2(CO)_6[P(OMe)_3]_2[S(C_7H_7)]_2$ (**19**)

6.2 Investigations with Tri(1-cyclohepta-2,4,6-trienyl) amine, $N(C_7H_7)_3$ (24), and Di(1-cyclohepta-2,4,6-trienyl) amine, $NH(C_7H_7)_2$ (25)

Tri(1-cyclohepta-2,4,6-trienyl) amine, $N(C_7H_7)_3$ (**24**), was prepared from tropylium bromide, C_7H_7Br, and ammonia gas. When using aqueous ammonia instead of the gas NH_3, di(1-cyclohepta-2,4,6-trienyl) amine, $NH(C_7H_7)_2$ (**25**), was obtained.



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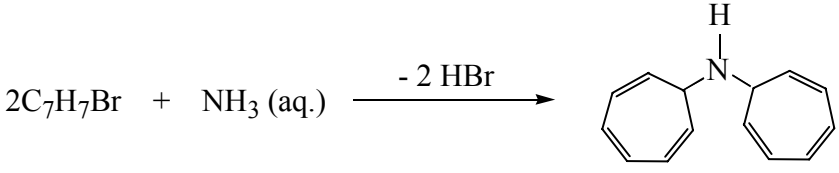
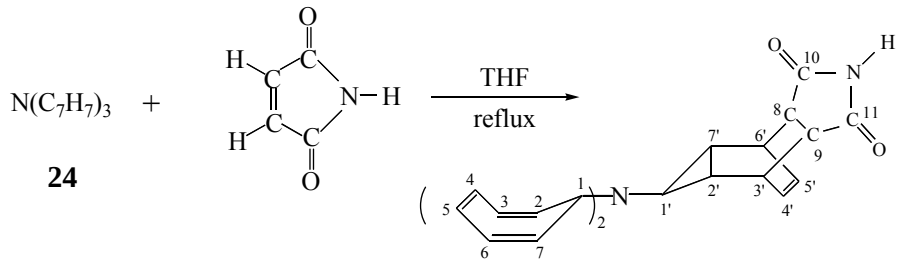
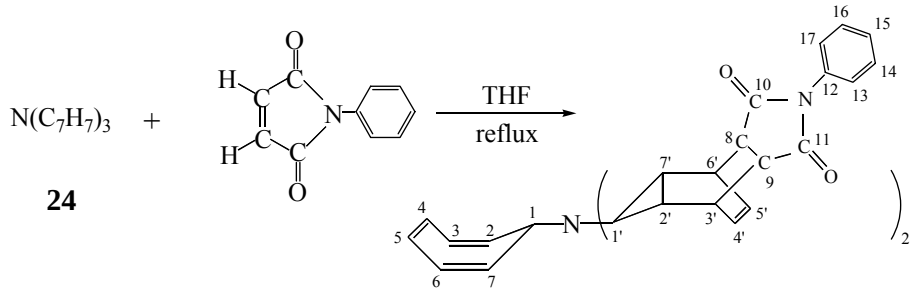


25

In analogy to the sulfane $S(C_7H_7)_2$ (**1**), tri(1-cyclohepta-2,4,6-trienyl) amine, $N(C_7H_7)_3$ (**24**), and di(1-cyclohepta-2,4,6-trienyl) amine, $NH(C_7H_7)_2$ (**25**), can undergo Diels-Alder reactions with maleimide and N-phenyl maleimide to give **26b**, **26c**, **27b** and **27c**, respectively.

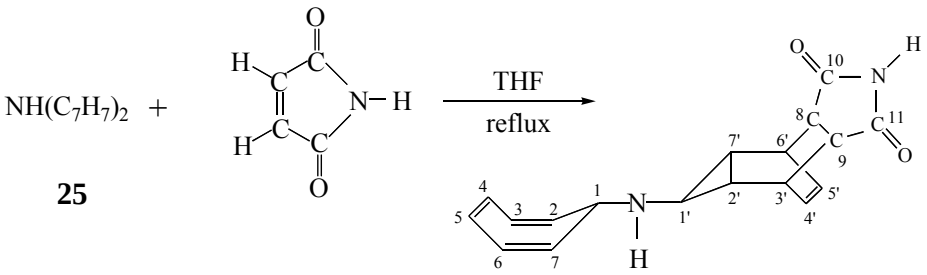


26b

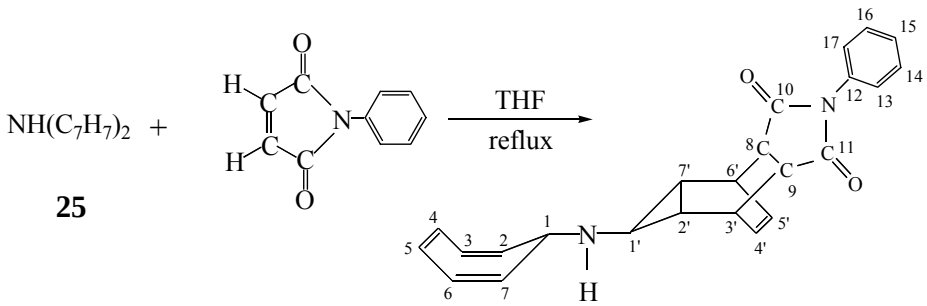


26c

Synthesis of the Diels-Alder adducts **26b** and **26c**



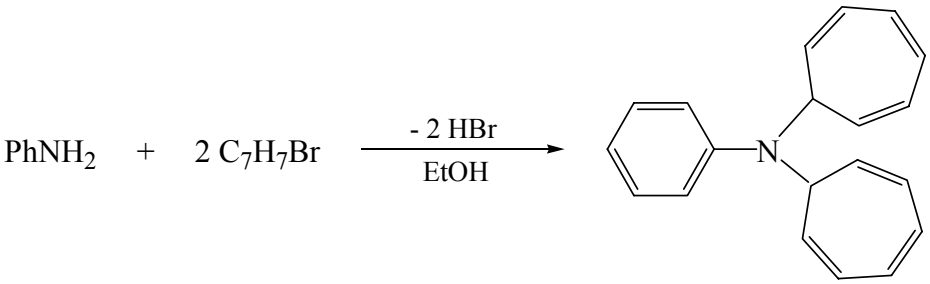
27b



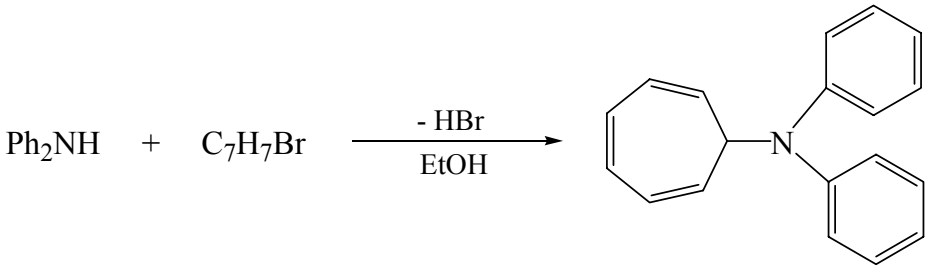
27c

Synthesis of the Diels-Alder adducts **27b** and **27c**

Similar to the synthesis of tri(1-cyclohepta-2,4,6-trienyl) amine, $N(C_7H_7)_3$ (**24**), and di(1-cyclohepta-2,4,6-trienyl) amine, $NH(C_7H_7)_2$ (**25**), the mixed tertiary amines di(1-cyclohepta-2,4,6-trienyl)phenylamine, $N(Ph)(C_7H_7)_2$ (**28**), and (1-cyclohepta-2,4,6-trienyl)diphenylamine, $N(Ph)_2(C_7H_7)$ (**29**) were prepared using aniline or diphenylamine.

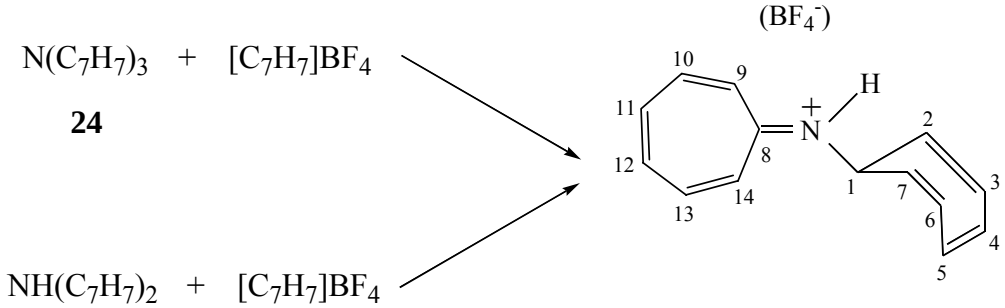


28



29

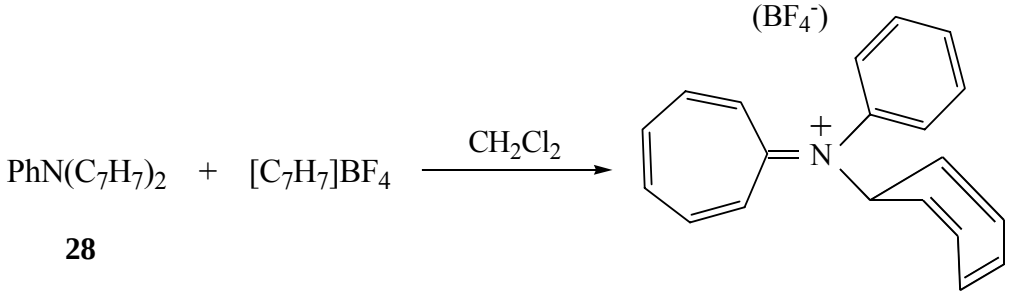
The reaction of $N(C_7H_7)_3$ (**24**) with $[C_7H_7]BF_4$ (1:1) leads to the N-tropylidene-N-(1-cyclohepta-2,4,6-trienyl)-immonium tetrafluoroborate salt, $[(C_7H_6)N(H)(C_7H_7)]BF_4$ (**30**). Compound **30** has also been obtained using $NH(C_7H_7)_2$ (**25**) as the educt.



30

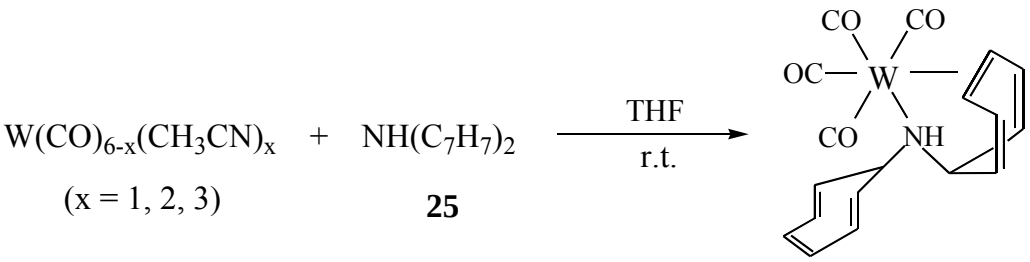
As expected, the tertiary amine $N(Ph)(C_7H_7)_2$ (**28**) reacted with $[C_7H_7]BF_4$ to give the dark-red salt $[(C_7H_6)N(Ph)(C_7H_7)]BF_4$ (**31**), in which one cyclohepta-2,4,6-trienyl ring is attached to the nitrogen atom in the boat conformation while the other ring is

connected to the nitrogen atom in a nearly planar tropylium-like conformation. Compared with compound **30**, the third position at the nitrogen atom in compound **31** was occupied by a phenyl group.



28 **31**

Attempts to use the amine $N(C_7H_7)_3$ (**24**) as a ligand in transition metal complexes were essentially unsuccessful. However, $NH(C_7H_7)_2$ (**25**) reacts with the mixture of tungsten(carbonyl)(acetonitrile) derivatives to give the chelate tetracarbonyl complex **32**, which is similar to the sulfane complexes **10** and **15**.



32

Compared with the versatile phosphane ligand tri(1-cyclohepta-2,4,6-trienyl) phosphane, $P(C_7H_7)_3$, the analogous amine $N(C_7H_7)_3$ (**24**) is unable to act as a coordination ligand, probably as a result of the steric shielding of the lone pair of electrons at the nitrogen atom. The sulfane $S(C_7H_7)_2$ (**1**) can act either as a sulfane two-electron ligand or as a chelating olefinic sulfane four-electron ligand, although the use of **1** is limited by its low thermal stability.

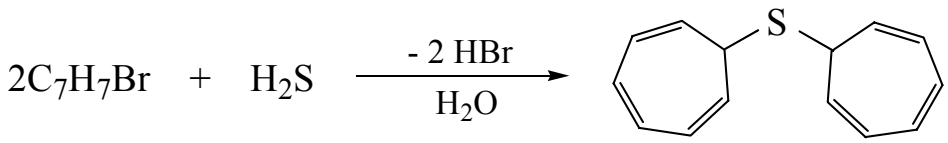
Chapter 7

Zusammenfassung

Die vorliegende Arbeit beschreibt die Synthese, Charakterisierung und Koordinationschemie von Di(1-cyclohepta-2,4,6-trienyl) thioether, $S(C_7H_7)_2$ (**1**), Tri(1-cyclohepta-2,4,6-trienyl)amin, $N(C_7H_7)_3$ (**24**), und Di(1-cyclohepta-2,4,6-trienyl)amin, $NH(C_7H_7)_2$ (**25**). Der potenziell mehrzähnige Ligand $S(C_7H_7)_2$ (**1**) zeigt eine vielseitige Koordinationschemie.

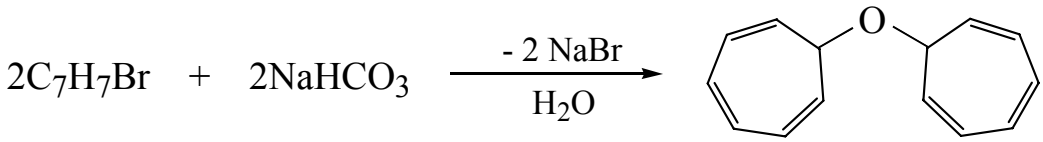
7.1 Untersuchungen an Di(1-cyclohepta-2,4,6-trienyl) thioether, $S(C_7H_7)_2$ (1)

Die Reaktion von Tropyliumbromid mit Schwefelwasserstoff-Gas führt zur Bildung des Sulfans **1**.

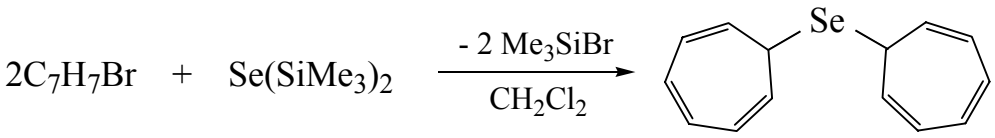


1

In ähnlicher Weise entsteht bei der Behandlung einer wäßrigen Lösung von Tropyliumbromid mit Natriumhydrogencarbonat der Di(1-cyclohepta-2,4,6-trienyl) ether.

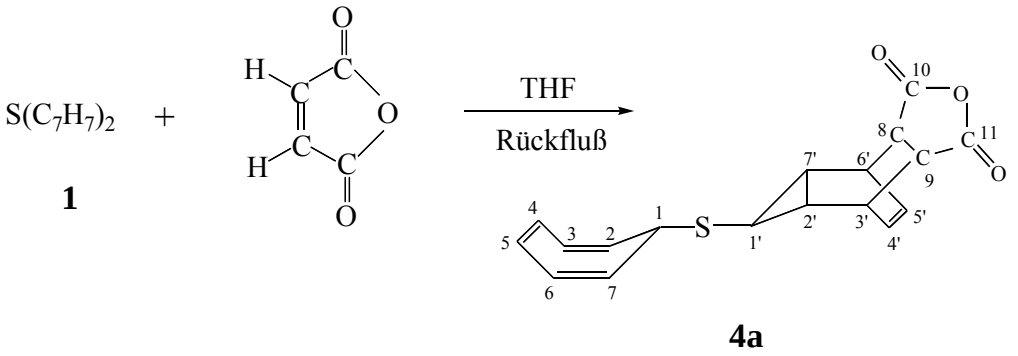


Nach einem Literaturbericht konnte Di(1-cyclohepta-2,4,6-trienyl) selenoether, $(C_7H_7)_2Se$ (**2**), aus Tropyliumbromid und gasförmigem Hydrogenselenid erhalten werden. Eine attraktive Alternative ist die Verwendung von Bis(trimethylsilyl) selenid als in-situ Quelle für H_2Se, in Analogie zur Synthese von Tri(1-cyclohepta-2,4,6-trienyl) phosphan aus Tris(trimethylsilyl) phosphan, $P(SiMe_3)_3$. Das Selan **2** wurde in guten Ausbeuten erhalten.

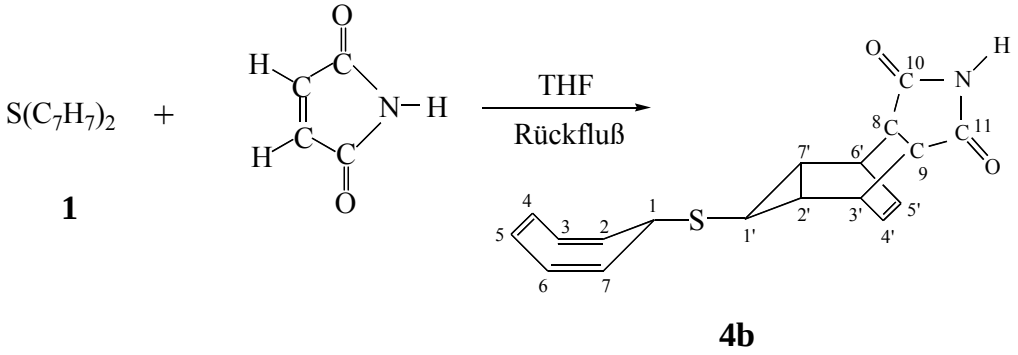


2

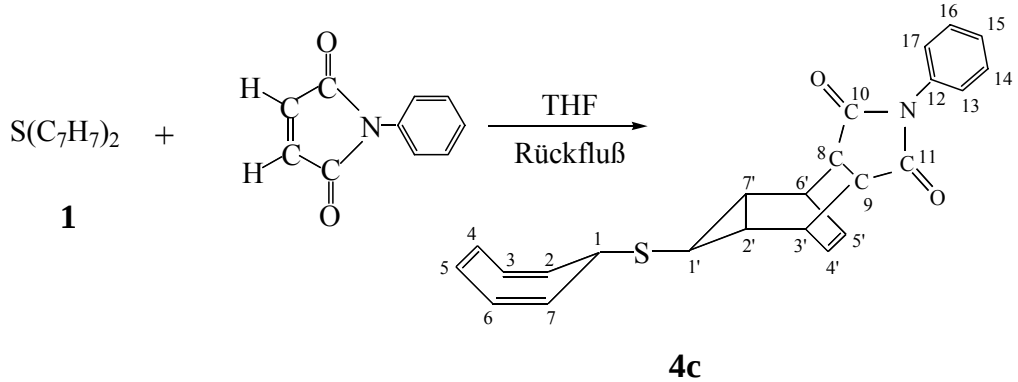
Di(1-cyclohepta-2,4,6-trienyl) thioether kann Diels-Alder Reaktionen mit Maleinsäureanhydrid, Maleinsäureimid und N-Phenylmaleinsäureimid eingehen. In den dabei entstehenden Verbindungen **4a**, **4b** und **4c** bleibt ein Cycloheptatrienylring intakt, während der zweite in die Diels-Alder Reaktion einbezogen wird.



1 **4a**



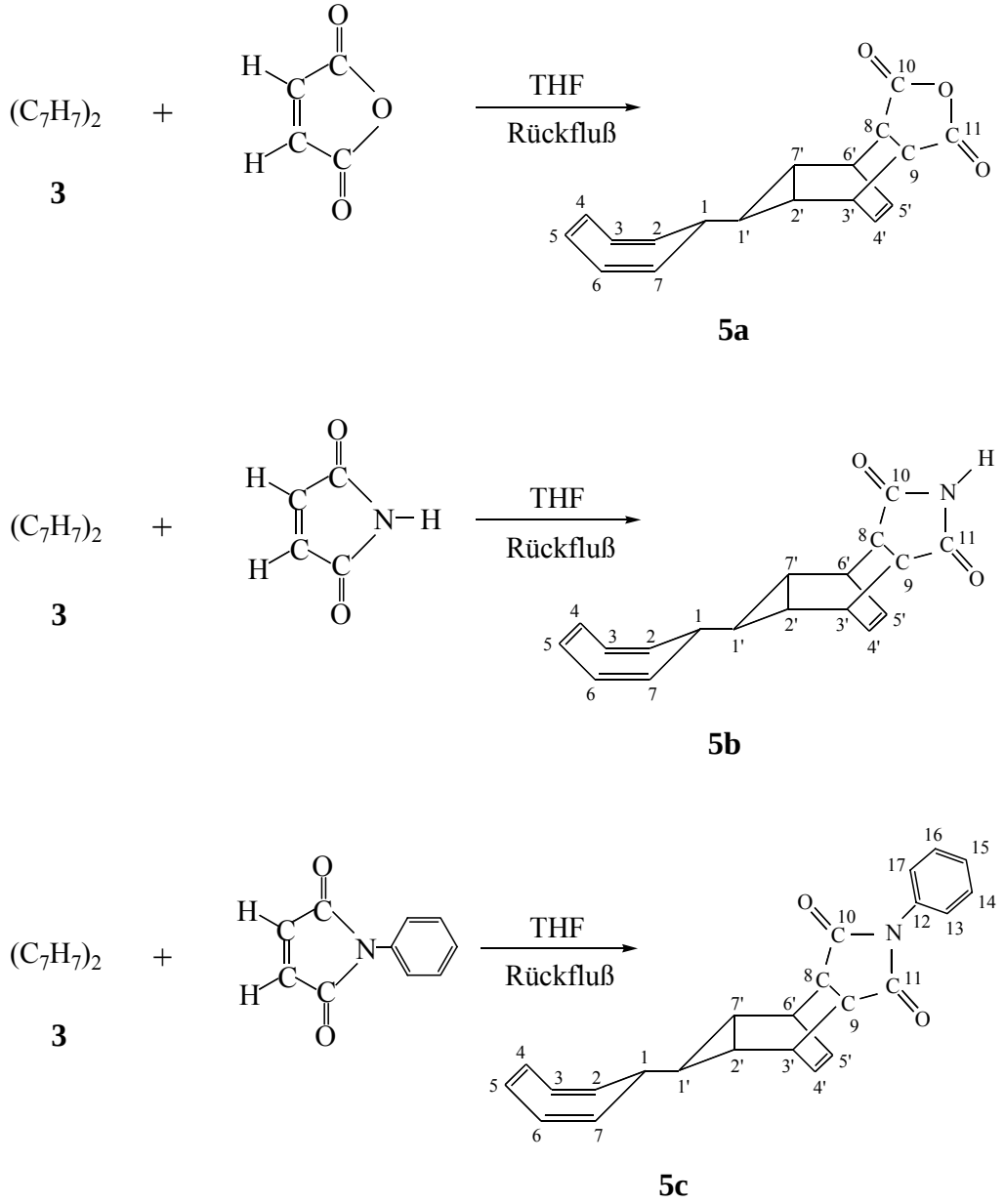
1 **4b**



1 **4c**

Synthese der Diels-Alder Addukte **4a**, **4b** und **4c**

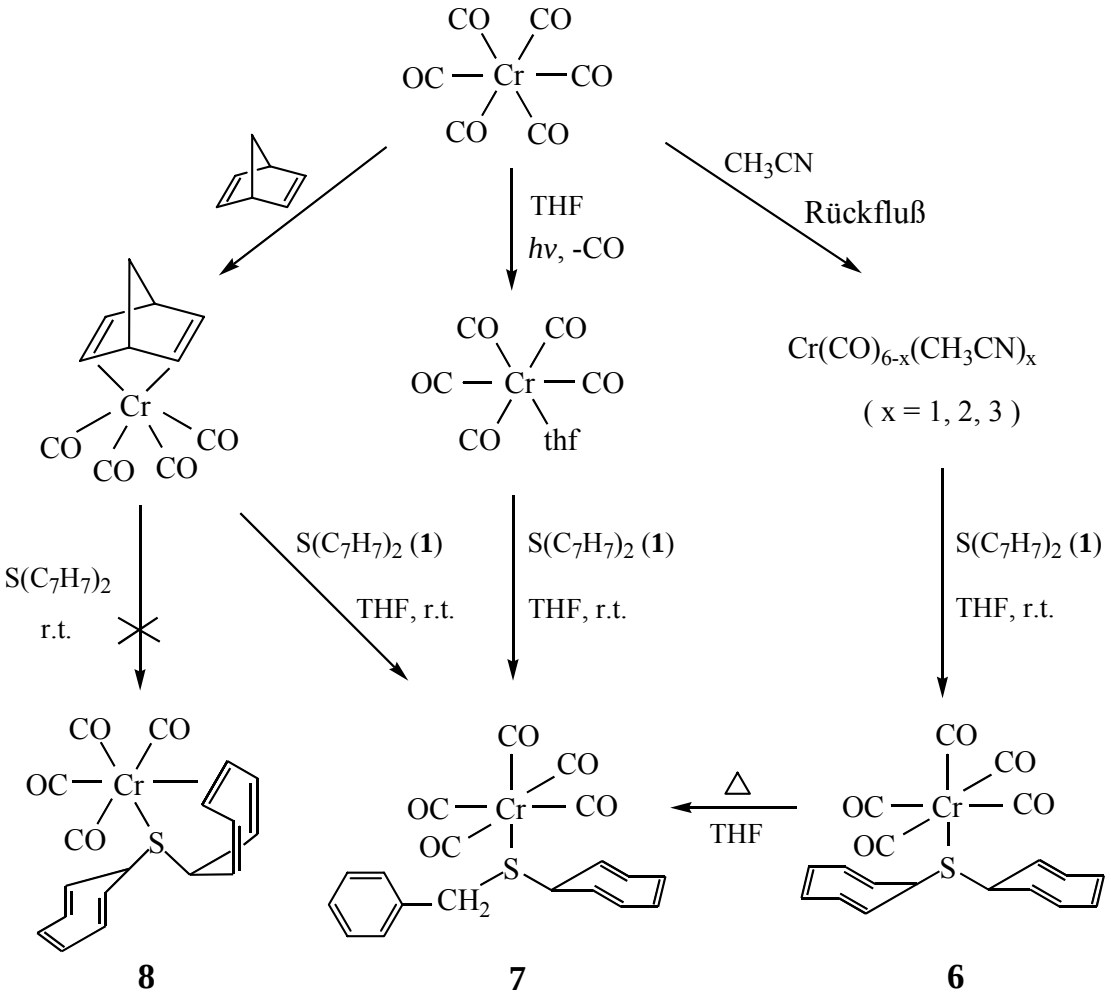
Zusätzlich wurden Diels-Alder Reaktionen von Ditropyl (**3**) mit Maleinsäureanhydrid, Maleinsäureimid und N-Phenylmaleinsäureimid durchgeführt. Die Produkte **5a**, **5b** und **5c** besitzen Strukturen, die denen der Verbindungen **4a**, **4b** und **4c** analog sind.



Synthese der Diels-Alder Addukte **5a**, **5b** und **5c**

Der Vorteil des potenziellen Liganden Di(1-cyclohepta-2,4,6-trienyl) thioether (**1**) im Vergleich zu anderen einfachen Sulfan-Liganden liegt in seiner Fähigkeit, als Chelatligand zu wirken, wobei die mittlere Doppelbindung eines der beiden siebengliedrigen Ringe an das Metallzentrum koordiniert wird. Der Nachteil liegt in seiner Oxidationsempfindlichkeit und der geringen thermischen Belastbarkeit.

Gegenüber den Komplexfragmenten $[M(CO)_{6-x}]$ (M = Cr, Mo, W; x = 1, 2), kann der potenzielle Ligand $S(C_7H_7)_2$ (**1**) als Zwei- oder als Vierelektronendonor fungieren. In Abhängigkeit von den sterischen Verhältnissen kann das Sulfan **1** auch umgelagert werden.

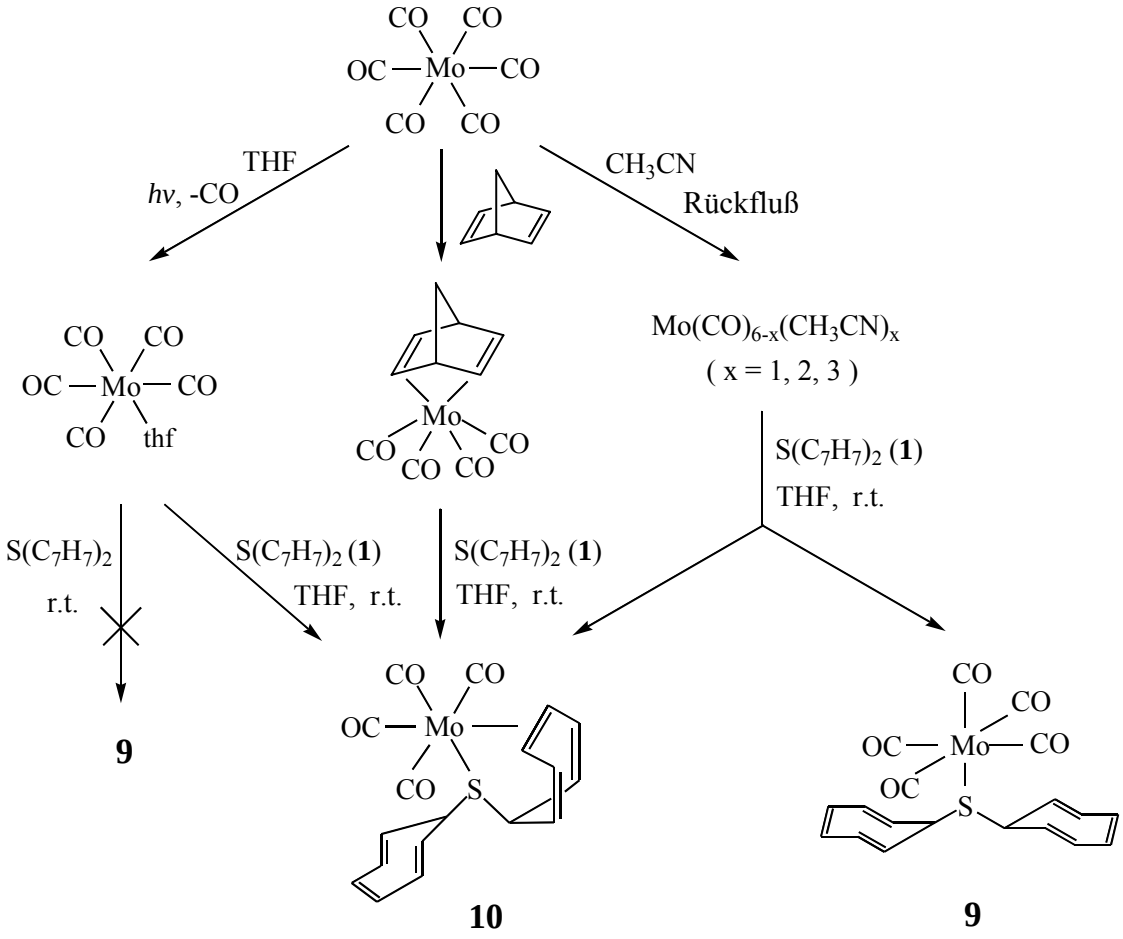


Synthese der Komplexe $Cr(CO)_5[S(C_7H_7)_2]$ (**6**) und $Cr(CO)_5[PhCH_2S(C_7H_7)]$ (**7**)

Bei der Reaktion von $Cr(CO)_5(thf)$ oder $Cr(CO)_4(\eta^4\text{-}C_7H_8)$ mit einem Äquivalent von **1** entsteht das monosubstituierte Derivat $Cr(CO)_5[PhCH_2S(C_7H_7)]$ (**7**), in welchem einer der siebengliedrigen Ringe unverändert geblieben ist, während der zweite in eine Benzylgruppe umgewandelt wurde. Aus einer Mischung von Chrom(carbonyl)(acetonitril)-Komplexen, $Cr(CO)_{6-x}(CH_3CN)_x$ (x = 1, 2, 3), konnte mit **1** der Komplex $Cr(CO)_5[S(C_7H_7)_2]$ (**6**) erhalten werden, in dem beide Cycloheptatrienylring-Substituenten frei beweglich am Schwefelatom hängen.

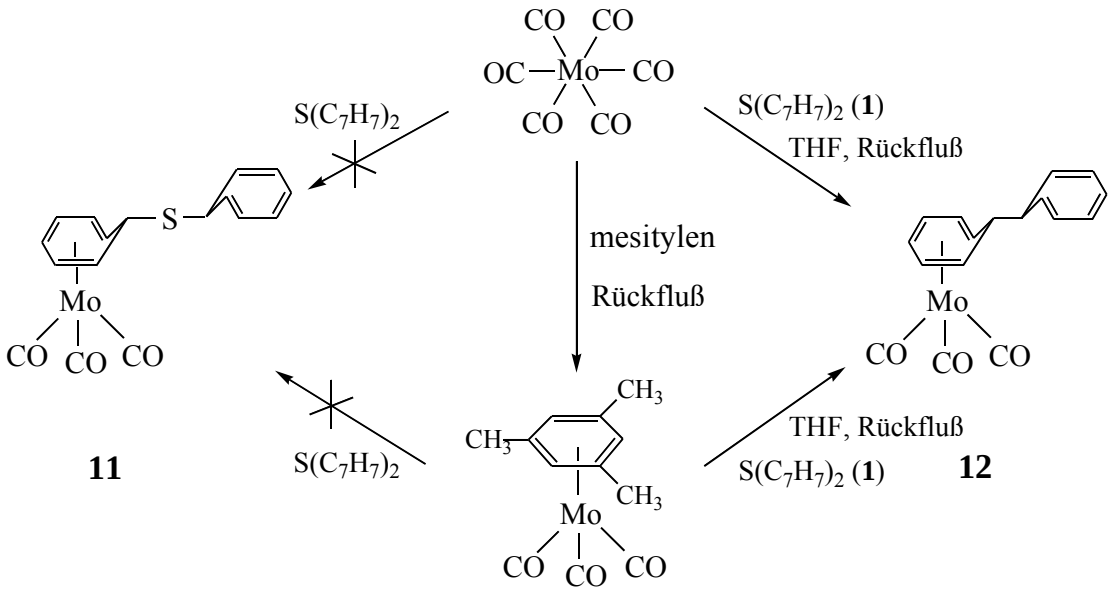
Mit der gleichen Methode wie bei den Chrom-Komplexen wurde aus $Mo(CO)_5(thf)$ oder $Mo(CO)_4(\eta^4\text{-}C_7H_8)$ und dem potenziellen Liganden **1** der Molybdän-Komplex

$Mo(CO)_4[(\eta^2\text{-}C_7H_7)S(C_7H_7)]$ (**10**) dargestellt. In diesem Komplex ist der Ligand Di(1-cyclohepta-2,4,6-trienyl) thioether über eines der freien Elektronenpaare am Schwefel und über die mittlere Doppelbindung eines Cycloheptatrienylrings an das Metallzentrum gebunden. $Mo(CO)_5[S(C_7H_7)_2]$ (**9**) konnte aus $Mo(CO)_{6-x}(CH_3CN)_x$ (x = 1, 2, 3) erhalten werden; in diesem Komplex ist der Sulfan-Ligand analog zu Komplex **6** wieder nur über ein freies Elektronenpaar am Schwefel an Molybdän gebunden.



Synthese der Komplexe $Mo(CO)_5[S(C_7H_7)_2]$ (**9**)
und $Mo(CO)_4[(\eta^2\text{-}C_7H_7)S(C_7H_7)]$ (**10**)

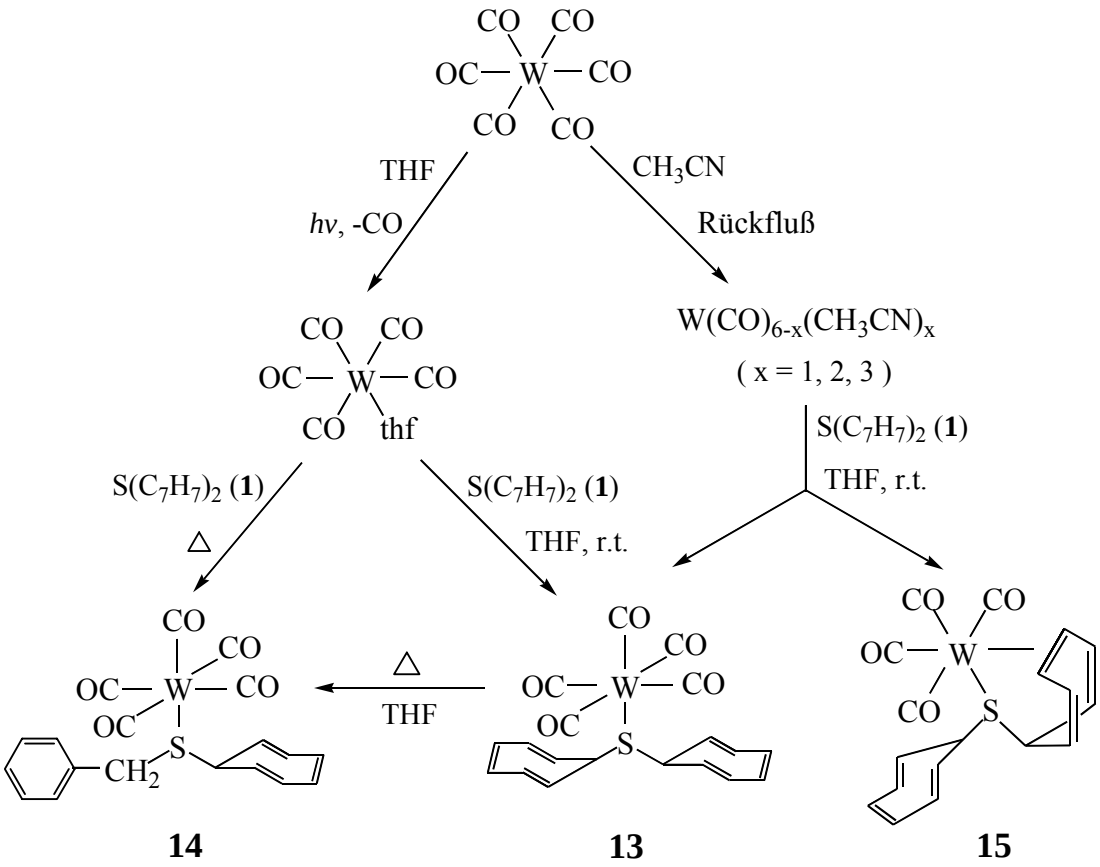
Hexacarbonylmolybdän reagiert mit Di(1-cyclohepta-2,4,6-trienyl) thioether (**1**) unter Zersetzung des Sulfan-Liganden und Bildung des Ditropyl-Komplexes (**12**). Dies zeigt die geringe Stabilität von **1** bei seinen Reaktionen mit Metallkomplexen.



Synthese des Komplexes $Mo(CO)_3[(\eta^6\text{-}C_7H_7)(C_7H_7)]$ (**12**)

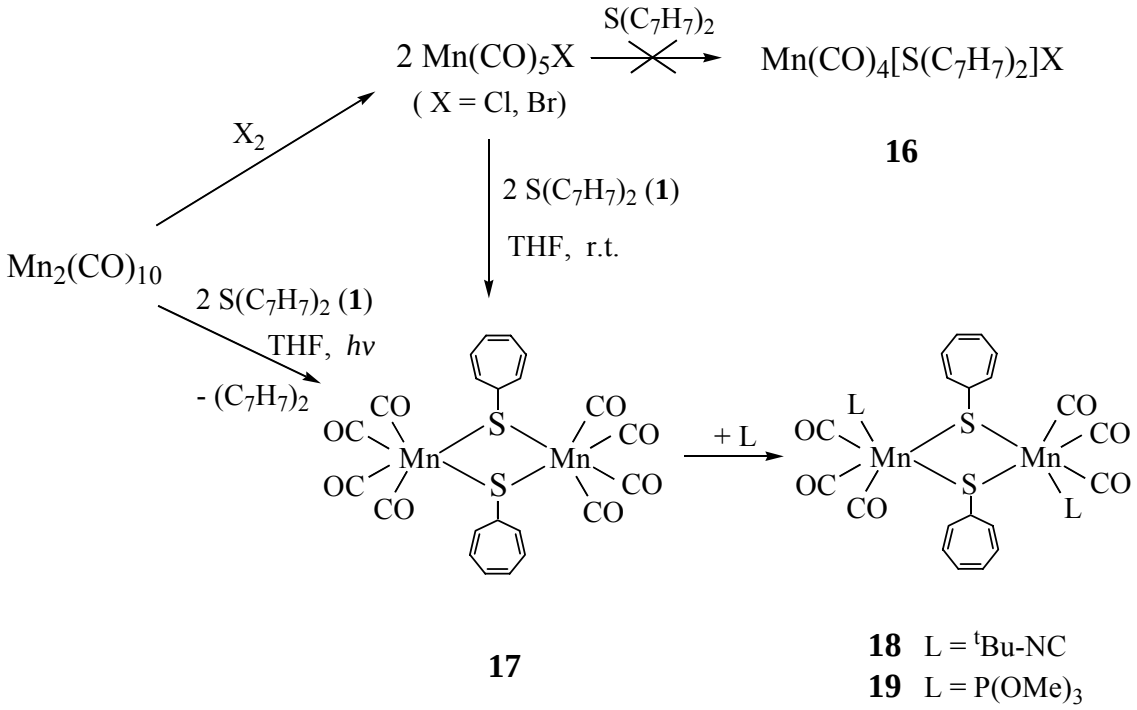
Aus dem Zwischenkomplex $W(CO)_5(thf)$ konnte bei der Umsetzung mit **1** der Pentacarbonylkomplex $W(CO)_5[S(C_7H_7)_2]$ (**13**) erhalten werden, der durch Erhitzen in THF-Lösung in den Benzyl-Komplex $W(CO)_5[PhCH_2S(C_7H_7)]$ (**14**) überführt wurde. Komplex **14** besitzt die gleiche Struktur wie der analoge Chromkomplex **7**.

Bei der Reaktion von Di(1-cyclohepta-2,4,6-trienyl) thioether (**1**) mit einem Gemisch von Wolfram(carbonyl)(acetonitril)-Komplexen, $W(CO)_{6-x}(CH_3CN)_x$ (x = 1, 2, 3), bildeten sich die Verbindungen $W(CO)_5[S(C_7H_7)_2]$ (**13**) und $W(CO)_4[(\eta^2\text{-}C_7H_7)S(C_7H_7)]$ (**15**), wobei **15** als Hauptprodukt vorlag. Der Wolframkomplex **15** besitzt die gleiche Struktur wie der entsprechende Molybdänkomplex **10**, in dem der Sulfan-Ligand ebenfalls als Vierelektronen-Donor auftritt und einen η^2-koordinierten neben einem freien Cyclohepta-2,4,6-trienyl-Substituenten am Schwefelatom trägt.



Synthese der Wolfram-Komplexe $W(CO)_5[S(C_7H_7)_2]$ (**13**), $W(CO)_5[PhCH_2S(C_7H_7)]$ (**14**) und $W(CO)_4[(\eta^2\text{-}C_7H_7)S(C_7H_7)]$ (**15**)

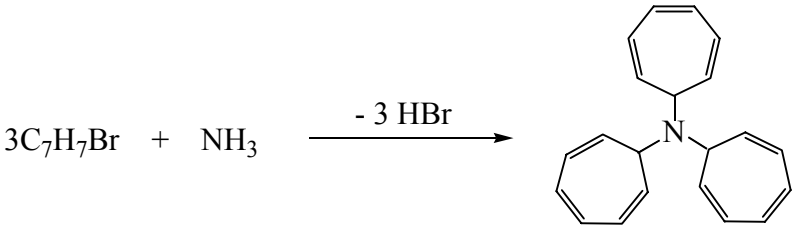
Ausgehend von Decacarbonyldimangan und Di(1-cyclohepta-2,4,6-trienyl) thioether (**1**) wurde der dimere Mangan-Komplex $Mn_2(CO)_8[S(C_7H_7)]_2$ (**17**) erhalten. Unter Bildung von Ditropyl sind zwei Cycloheptatrienylsulfido-Gruppen entstanden, die als Brückenliganden die beiden Mangan-Zentren zusammenhalten. Komplex **17** konnte auch aus Pentacarbonylmangan-halogeniden, $Mn(CO)_5X$ (X = Cl, Br), dargestellt werden. Es war zudem möglich, zwei Carbonylgruppen durch stärkere σ-Donor-π-Akzeptor-Liganden wie *tert*-Butylisocyanid oder Trimethylphosphit zu ersetzen, wobei die Komplexe $Mn_2(CO)_6[^tBuNC]_2[S(C_7H_7)]_2$ (**18**) und $Mn_2(CO)_6[P(OMe)_3]_2[S(C_7H_7)]_2$ (**19**) entstanden.



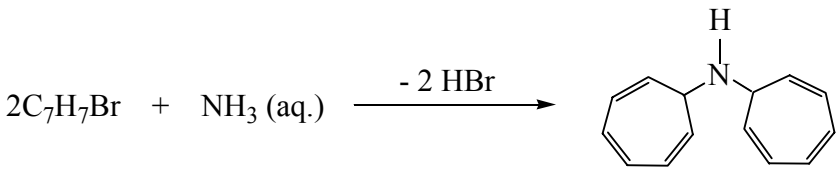
Synthese der Mangankomplexe $Mn_2(CO)_8[S(C_7H_7)]_2$ (**17**), $Mn_2(CO)_6[^tBuNC]_2[S(C_7H_7)]_2$ (**18**) und $Mn_2(CO)_6[P(OMe)_3]_2[S(C_7H_7)]_2$ (**19**)

7.2 Untersuchungen an Tri(1-cyclohepta-2,4,6-trienyl)amin, $N(C_7H_7)_3$ (24), und Di(1-cyclohepta-2,4,6-trienyl)amin, $NH(C_7H_7)_2$ (25)

Tri(1-cyclohepta-2,4,6-trienyl)amin, $N(C_7H_7)_3$ (**24**), wurde durch Umsetzung von Tropyliumbromid mit gasförmigem Ammoniak hergestellt. Wenn anstatt des Gases NH_3 wässrige Ammoniaklösung eingesetzt wurde, entstand Di(1-cyclohepta-2,4,6-trienyl)amin, $NH(C_7H_7)_2$ (**25**).

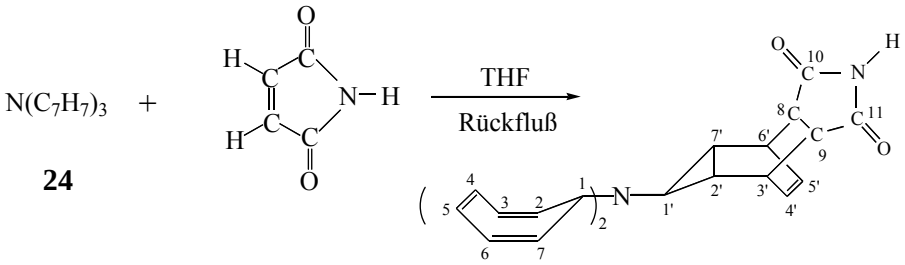


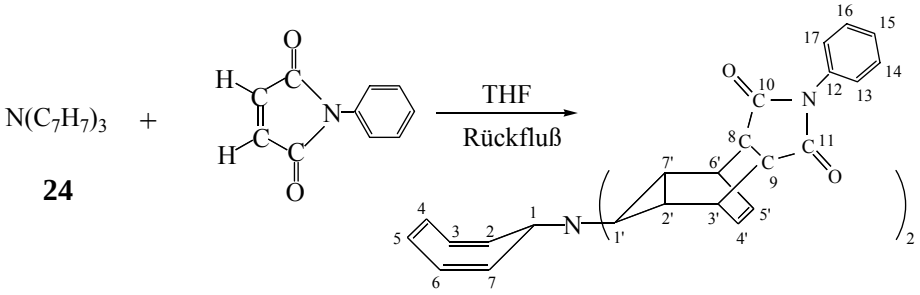
24



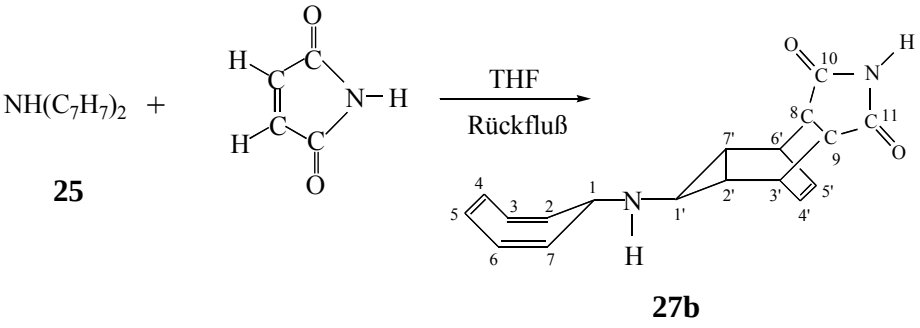
25

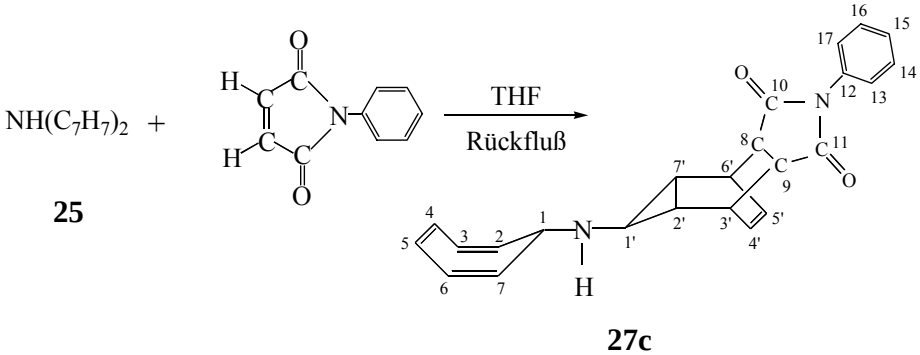
Tri(1-cyclohepta-2,4,6-trienyl)amin, $N(C_7H_7)_3$ (**24**), und Di(1-cyclohepta-2,4,6-trienyl)amin, $NH(C_7H_7)_2$ (**25**), können wie das entsprechende Sulfan $S(C_7H_7)_2$ (**1**) Diels-Alder Additionen mit Maleinsäureimid und N-Phenylmaleinsäureimid eingehen, wobei sich die Verbindungen **26b**, **26c**, **27b** und **27c** bilden.





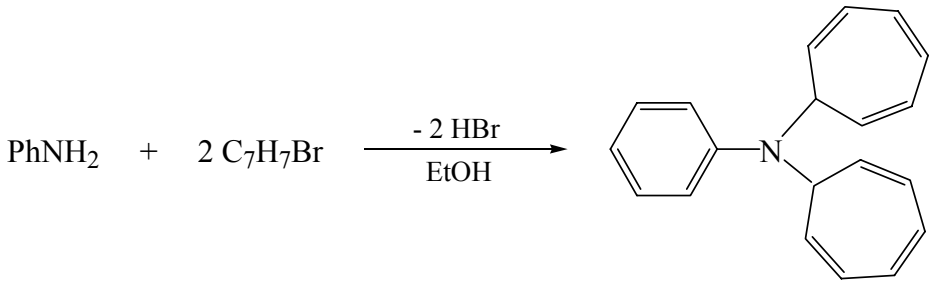
Synthese der Diels-Alder Addukte **26b** and **26c**





Synthese der Diels-Alder Addukte **27b** and **27c**

Ähnlich wie bei der Synthese von **24** und **25** konnten die gemischt-substituierten tertiären Amine **28** und **29** mit Cycloheptatrienyl- und Phenylringen aus Anilin oder Diphenylamin und Tropyliumbromid hergestellt werden.



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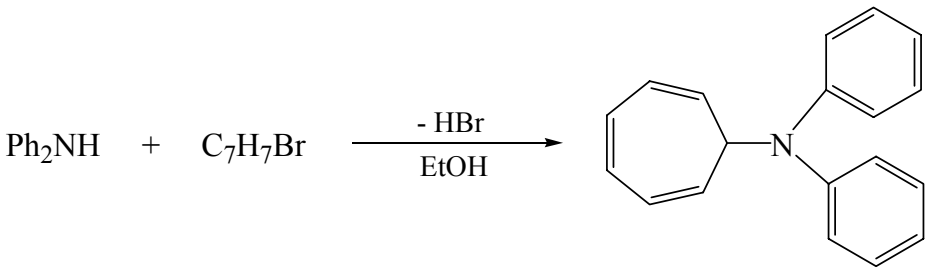
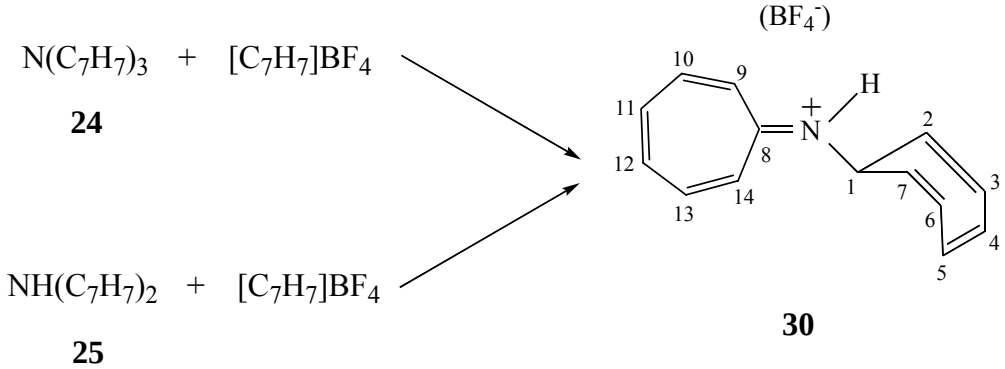


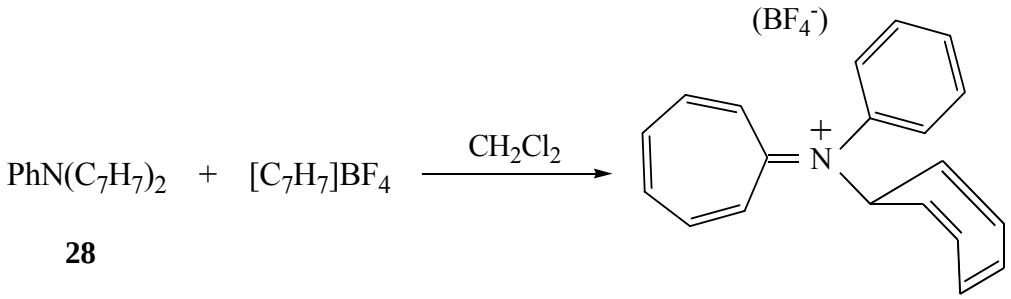
29

Die Reaktion von Tri(1-cyclohepta-2,4,6-trienyl)amin (**24**) oder Di(1-cyclohepta-2,4,6-trienyl)amin (**25**) mit Tropylium-tetrafluoroborat führt nicht zu einer Quaternisierung des Aminostickstoff-Atoms, sondern resultiert in der Bildung des Immoniumsalzes (**30**).



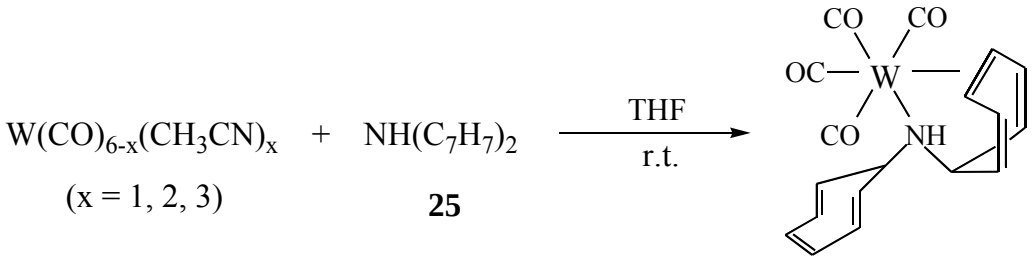
30

Wie erwartet reagierte auch das tertiäre Amin $PhN(C_7H_7)_2$ (**28**) mit Tropylium-tetrafluoroborat unter Hydridübertragung, wobei das dunkelrote Immoniumsalz $[(C_7H_6)N(Ph)(C_7H_7)]BF_4$ (**31**) erhalten wurde. Wie die Immoniumverbindung **30** besitzt auch **31** einen Cycloheptatrienylring in der Wannenform sowie einen nahezu planaren Siebenring.



28 **31**

Schließlich sollte Tri(1-cyclohepta-2,4,6-trienyl)amin (**24**) auf seine Eignung als Komplexligand untersucht werden. Alle hierzu durchgeführten Versuche verliefen erfolglos. Jedoch konnte Di(1-cyclohepta-2,4,6-trienyl)amin (**25**) mit einem Gemisch aus Wolfram(carbonyl)(acetonitril)-Komplexen, $W(CO)_{6-x}(CH_3CN)_x$ (x = 1, 2, 3), zur Reaktion gebracht werden, wobei der Chelatkomplex **32** gebildet wurde, der den Sulfankomplexen **8**, **10** und **15** ähnlich ist.



32

Im Vergleich zu dem vielseitigen Phosphanliganden Tri(1-cyclohepta-2,4,6-trienyl)phosphan, $P(C_7H_7)_3$, ist das analoge Amin $N(C_7H_7)_3$ (**24**) nicht in der Lage, als Koordinationsligand zu fungieren, vermutlich wegen der sterischen Abschirmung des freien Elektronenpaares am Stickstoffatom. Das Sulfan $S(C_7H_7)_2$ (**1**) kann entweder als Zweielektronen-Ligand oder als olefinischer Vierelektronen-Chelatligand wirken, obwohl die Verwendung von **1** wegen seiner geringen thermischen Stabilität begrenzt ist.

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Erklärung

Hiermit erkläre ich, dass ich die Arbeit selbständig verfasst und keine anderen als die von mir angegebenen Hilfsmittel benutzt habe.

Ferner erkläre ich, dass ich nicht anderweitig mit oder ohne Erfolg versucht habe, eine Dissertation einzureichen oder mich der Doktorprüfung zu unterziehen.

Bayreuth, den ....